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Photochemical Studies of Dinuclear Methylene-Bridged Transition-Metal Complexes

Dissertation

Presented in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in the Graduate School of the Ohio State University

By

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****

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1995

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To Mom, Dad, and Justin
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"Matrix Photochemistry of trans-[Cp*Fe(CO)]_2(μ-CO)(μ-CH_2): Generation
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FIELDS OF STUDY

Major Field: Chemistry

Experimental Organometallic Chemistry.
The Ohio State University; Professor Bruce E. Bursten, Advisor.
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<td>3MP</td>
<td>(CH₃CH₂)₂CHCH₃</td>
<td>3-methylpentane</td>
</tr>
<tr>
<td>C-N₂</td>
<td>Cooled N₂</td>
<td>Cooled nitrogen</td>
</tr>
<tr>
<td>Carbitol</td>
<td>C₆H₁₀O(CH₂)₆OCH₂CH₂OH</td>
<td>2-(2-Ethoxyethoxy)ethanol</td>
</tr>
<tr>
<td>Decalin</td>
<td>C₁₀H₁₈</td>
<td>Decahydronaphthalene</td>
</tr>
<tr>
<td>Diazald</td>
<td>CH₃C₆H₄SO₂N(CH₃)NO</td>
<td>N-methyl-N-nitroso-p-toluenesulfonamide</td>
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<tr>
<td>DMAD</td>
<td>(CH₃O₂C)C≡C(CO₂CH₃)</td>
<td>Dimethyl acetylenedicarboxylate</td>
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<tr>
<td>Cp</td>
<td>C₅H₅</td>
<td>Cyclopentadienyl</td>
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<td>Cp'</td>
<td>C₆H₄CH₃</td>
<td>Methylcyclopentadienyl</td>
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<td>Cp⁺</td>
<td>C₅(CH₃)₅</td>
<td>Pentamethylcyclopentadienyl</td>
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<tr>
<td>dppp</td>
<td>Ph₂P(CH₂)₃PPh₂</td>
<td>1,3-Bis(diphenylphosphino) propane</td>
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<tr>
<td>E-N₂</td>
<td>Evaporated N₂</td>
<td>Evaporated nitrogen</td>
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<tr>
<td>Glyme</td>
<td>CH₃OCH₂CH₂OCH₃</td>
<td>1, 2-Dimethoxyethane</td>
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<tr>
<td>IPA</td>
<td>(CH₃)₂CHOH</td>
<td>Isopropyl alcohol</td>
</tr>
<tr>
<td>LN₂</td>
<td>Liquid N₂</td>
<td>Liquid nitrogen</td>
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<tr>
<td>MA</td>
<td>HOOCCH=CHCOOH</td>
<td>Maleic anhydride</td>
</tr>
<tr>
<td>MCH</td>
<td>C₉H₁₁CH₃</td>
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<tr>
<td>Me</td>
<td>CH₃</td>
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<tr>
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<td>CH₂CH₂CH₂CH₃</td>
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<td>Ph</td>
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<td>Phenyl</td>
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<tr>
<td>PHAC</td>
<td>C₆H₅C≡CH</td>
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</tr>
<tr>
<td>Pr</td>
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<td>Propyl</td>
</tr>
<tr>
<td>THF</td>
<td>C₄H₈O</td>
<td>Tetrahydrofuran</td>
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LIST OF INSTRUMENTAL ABBREVIATIONS

<table>
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<tbody>
<tr>
<td>EI</td>
<td>Electron ionization</td>
</tr>
<tr>
<td>ESR</td>
<td>Electron spin resonance</td>
</tr>
<tr>
<td>FAB</td>
<td>Fast atom bombardment</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>LFP</td>
<td>Laser flash photolysis</td>
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<tr>
<td>MAS</td>
<td>Magic angle spinning</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrum</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>OMA</td>
<td>Optical multichannel analyzer</td>
</tr>
<tr>
<td>UV-vis</td>
<td>Ultraviolet-visible</td>
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# LIST OF DEFINITIONS

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<tr>
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<th>Definition</th>
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<tr>
<td>FPT</td>
<td>freeze-pump-thaw</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>hvSOLN</td>
<td>Spectrum of irradiated solution (LT)</td>
</tr>
<tr>
<td>LT</td>
<td>Low temperature</td>
</tr>
<tr>
<td>LTSOLN</td>
<td>Low temperature solution spectrum</td>
</tr>
<tr>
<td>LTSOLV</td>
<td>Low temperature solvent spectrum</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>RTSOLN</td>
<td>Room temperature solution spectrum</td>
</tr>
<tr>
<td>RTSOLV</td>
<td>Room temperature solvent spectrum</td>
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Chapter I

Introduction

In 1926, Fischer and Tropsch\textsuperscript{1} proposed that the reaction of CO and H\textsubscript{2} on appropriate metal surfaces proceeds through "polymerization of methylene groups" on the surface of the metal. These methylene groups were proposed to form from reduction of the carbon atoms after decomposition of CO had occurred on the metal surface. This process, the Fischer-Tropsch reaction (Figure 1.1), produces hydrocarbons and olefins, among others, depending on the catalyst and the conditions employed.\textsuperscript{2}

Dinuclear methylene-bridged transition-metal complexes have received a great deal of attention\textsuperscript{3} since Herrmann synthesized the first complex of this class, \([\text{CpMn(CO)}\text{2}]\text{2(\text{\textmu-CH}}_2)\text{)}\text{ (Cp = \eta}^5\text{-C}_5\text{H}_5\text{).}\textsuperscript{4} The interest in these compounds has been primarily the result of the possibility that M-M bonds with alkylidene bridges were intermediates in the Fischer-Tropsch reaction.

Support of the \text{CH}2-linking mechanism of the Fischer-Tropsch reaction has been obtained through modeling studies of the reaction of
Figure 1.1: Proposed mechanism of the Fischer-Tropsch reaction.¹
CH$_2$N$_2$ with Fe, Ru, Co, Ni, and Pd surfaces which produced C$_2$ to C$_{18}$ alkanes and mono-olefins.$^{2d, e, f}$ Brady and Pettit studied the reaction of CH$_2$N$_2$ with and without H$_2$ over Co, Fe, Ru, Ni, Pd, and Cu surfaces. Without H$_2$ in the CH$_2$N$_2$ reaction mixture, only ethylene and nitrogen gas were produced at 1 atmosphere between 25 and 200°C. However, when H$_2$ was added to the reaction mixture, hydrocarbons ranging from C$_1$ to C$_{18}$ were produced when using Co, Fe, or Ru metals. In addition, the distribution of four-C hydrocarbon species produced with CH$_2$N$_2$ at 210°C is very similar to the four-C hydrocarbon species produced when CO and H$_2$ are reacted at 210°C over the same catalyst. The similarities in product distributions suggest a similar mechanism; thus, the chemical behavior of methylene complexes may provide insight into this process.$^{2d}$ Copperthwaite and coworkers have obtained X-ray photoelectron spectroscopic evidence for the formation of a C-C bond through the interaction of adsorbed CO and methylene on iron surfaces.$^{2e}$

Carbon-carbon bond formation has been observed in the reaction of [CpCo(CO)]$_2$(μ-CH$_2$) with ethylene, which yields propene and CpCo(CO)(C$_2$H$_4$). Bergman and Theopold proposed that an unsaturated
cobalt complex, [Cp(CO)Co(μ-CH₂)CoCp], functions as an autocatalyst in the reaction mechanism.⁵

The methylene-bridged species in this study are [CpCo(CO)]₂(μ-CH₂) and [CpMn(CO)]₂(μ-CH₂) (Figure 1.2). The electronic structure of both molecules has been studied extensively. Molecular orbital calculations indicate that the methylene carbon has an overall negative charge.⁶,⁷ᵃ These computational results have been substantiated by UV-photoelectron spectroscopy of [CpMn(CO)]₂(μ-CH₂) by showing that the relative intensities of the ionization bands are consistent with a charge transfer from the metals to the methylene.⁷ᵃ In addition the binding energy data of the μ-CH₂ groups of [CpMn(CO)]₂(μ-CH₂) and [CpCo(CO)]₂(μ-CH₂), as determined by X-ray photoelectron spectroscopy, are below the binding energy of cyclopropane.⁷ᵇ This low binding energy

![Figure 1.2: [CpCo(CO)]₂(μ-CH₂) and [CpMn(CO)]₂(μ-CH₂).](image-url)
suggests that the bridging methylene groups may be highly negatively charged. An electron density study of \([\text{CpMn(CO)}_2\mu-\text{CH}_2]\) by X-ray electron diffraction also shows the carbon to be situated in a region of negative charge. Finally, the \(^{13}\text{C}\) and \(^1\text{H}\) proton NMR resonances are shifted upfield from their mononuclear (M-CHR) analogs roughly reflecting a higher electron density on the methylene carbon atom.

This increased electron density on the methylene carbon can be rationalized from the molecular orbital diagram obtained from the frontier orbitals. Figure 1.3 shows the interactions of the HOMO and LUMO orbitals of \([\text{CpMn(CO)}_2\mu-\text{CH}_2]\) with the frontier orbitals of the methylene fragment. Clearly the \([\text{CpMn(CO)}_2\mu-\text{CH}_2]\) LUMO has the correct symmetry to interact with the filled \(a_1\) orbital of \(\text{CH}_2\). Further, the HOMO has the proper symmetry to interact with the empty \(p\pi\) orbital of \(\text{CH}_2\). The negatively charged methylene group indicates that the bridging methylene is a better acceptor than donor ligand. Thus, the donation from the metal fragment HOMO to the \(p\pi\) \(\text{CH}_2\) orbital could be described as an effective charge transfer.

These molecular orbital results suggest that the lowest electronic excitation in these molecules, roughly defined as the HOMO to LUMO transition, will be localized within the M-C-M ring. Experimentally, these
Figure 1.3: A portion of the molecular orbital diagram of $[\text{CpMn(CO)}_2]_2(\mu-\text{CH}_2)$, showing the interaction of the frontier orbitals of $\text{CH}_2$ with those of $[\text{CpMn(CO)}_2]_2$.\textsuperscript{7a}
complexes have been shown to undergo reversible oxidation and reduction, although the resultant cations and anions are unstable. The stability of the resultant radical cation depended on the nature of the metal and bridge substituents. The oxidation and reduction potentials of $[\text{CpCo(CO)}]_2(\mu-\text{CH}_2)$ and $[\text{CpMn(CO)}]_2(\mu-\text{CH}_2)$ also varied. Finally, $[\text{CpCo(CO)}]_2(\mu-\text{CH}_2)$ and $[\text{CpMn(CO)}]_2(\mu-\text{CH}_2)$ exhibit different colors, red and green, respectively, which indicate differences in the energetics of their electronic transitions. Thus, although their electronic structure is fundamentally similar, there are differences which may manifest themselves in slightly different photoreactivities.

In considering the photoreactivity of $[\text{CpCo(CO)}]_2(\mu-\text{CH}_2)$ and $[\text{CpMn(CO)}]_2(\mu-\text{CH}_2)$, one must consider the larger genre of dinuclear species from which they are derived, namely the dinuclear cyclopentadienyl carbonyl transition-metal complexes. This class of compounds exhibits a rich photochemistry, as is perhaps best exemplified by $[\text{CpFe(CO)}(\mu-\text{CO})]_2$. Initial studies on $[\text{CpFe(CO)}(\mu-\text{CO})]_2$ showed the photochemical production of the 17 electron $\text{CpFe(CO)}_2^*$ radical. Evidence for the production of radicals was provided by the photochemical reaction of $[\text{CpFe(CO)}(\mu-\text{CO})]_2$ with $\text{CCl}_4$, in which the product $\text{CpFe(CO)}_2\text{Cl}$ was isolated. The formation $\text{CpFe(CO)}_2\text{Cl}$ is consistent with homolytic
cleavage of the M-M bond into 2 CpFe(CO)$_2^*$ radicals, followed by halogen abstraction (Figure 1.4).\textsuperscript{11}

![Diagram](image)

Figure 1.4: [CpFe(CO)(μ-CO)]$_2$, CCl$_4$ and hv.

Irradiation of [CpFe(CO)(μ-CO)]$_2$ and PPh$_3$ resulted in the formation of the photosubstitution product, Cp(CO)Fe(μ-CO)$_2$Fe(PPh$_3$)Cp (Figure 1.5). Tyler, Schmidt, and Gray proposed a mechanism for this reaction that involved a dinuclear intermediate with one saturated 18 electron metal center and one unsaturated 16 electron metal center. In this mechanism (Figure 1.6) the phosphine first binds to the intermediate, followed by CO dissociation to yield the final product.\textsuperscript{12}

![Diagram](image)

Figure 1.5: [CpFe(CO)(μ-CO)]$_2$, PPh$_3$, and hv.
Figure 1.6: The mechanism for phosphine photosubstitution of $[\text{CpFe(CO)(\mu-CO)}]_2$ proposed by Tyler, Schmidt, and Gray.\textsuperscript{12}
Laser flash photolysis (LFP) work by Casper and Meyer confirmed the formation of two species upon the photolysis of [CpFe(CO)(μ-CO)]₂, one short-lived ($t_{1/2}$ ca. 25 μs)\(^{13,14}\) and the other was long-lived ($t_{1/2}$ ca. 3 s).\(^{14,15,16}\) These species were detected by UV-vis spectroscopy; thus, no structural information was obtained. The short-lived species was identified as CpFe(CO)₂ radical, while the nature of the long-lived species was unknown.\(^{14}\)

Low temperature matrix isolation studies\(^{16,17}\) and transient infrared studies\(^{15,18}\) have not supported the all terminal intermediate proposed by Tyler, Schmidt, and Gray. Photolysis of [CpFe(CO)₂(μ-CO)]₂ in 90% methylcyclohexane (MCH)/10% 3-methylpentane (3MP) at 77 K yielded CO vibrational bands at 2132 and 1811 cm\(^{-1}\). The 2132 cm\(^{-1}\) band was assigned to free CO while the 1811 cm\(^{-1}\) resonance inferred a dinuclear species with at least one bridging CO group.\(^{16,17}\) Thus, a triply bridged species, [CpFe]₂(μ-CO)₃ (Figure 1.7), was assigned to the long-lived intermediate of the earlier LFP experiment. Transient solution IR studies demonstrated production of this species at room temperature, at which its IR band was found at 1823 cm\(^{-1}\) in cyclohexane.\(^{15}\)

High energy irradiation favors the formation of the CO-loss species while low energy photons favor homolytic cleavage into mononuclear
The two primary photoprocesses of \([\text{CpFe(CO)(\mu-CO)\text{]}}\)\text{\textsubscript{2}} are shown in Figure 1.8. Other studies have observed other transients, including a double-CO-loss species, \([\text{CpFe(CO)\text{]}}\)\text{\textsubscript{2}}.\text{\textsuperscript{18,20,21}} \text{[CpFe}\text{]}\text{\textsubscript{2}}(\text{p-CO})\text{\textsubscript{3}} reacts with phosphines and other two electron donors by an associative bimolecular mechanism derived from a large negative \(\Delta S^\ddagger\) value.\textsuperscript{15a,22,23} This mechanism has also been suggested in the reactions of \([\text{CpFe}\text{]}\text{\textsubscript{2}}(\text{\mu-CO})\text{\textsubscript{3}} with alkynes. The product ratios of alkyne competition reactions with \([\text{CpFe}\text{]}\text{\textsubscript{2}}(\text{\mu-CO})\text{\textsubscript{3}}, determined by HPLC, show close agreement to the respective kinetic rate ratios. Therefore, a connection can be established between the kinetic results obtained, in our case, mostly by LFP, and the insertion products. As in the phosphine case, the large negative \(\Delta S^\ddagger\) values found in the \([\text{CpFe}\text{]}\text{\textsubscript{2}}(\text{\mu-CO})\text{\textsubscript{3}} and alkyne reactions indicates an associative bimolecular mechanism, supporting an identical mechanism for alkyne insertion (Figure 1.9) and
Figure 1.8: Two primary photochemical pathways of \([\text{CpFe(CO)}(\mu-\text{CO})]\_2\).
phosphine substitution. Alkyne insertion is proposed to follow the initial \( \eta^2 \)-alkyne substitution onto \([\text{CpFe}]_2(\text{CO})_3\). Figure 1.10 shows the proposed mechanism of photochemical substitution of two electron donors (i.e. phosphines) and alkynes with \([\text{CpFe}(\text{CO})(\mu-\text{CO})]_2\). Zhang and Brown have observed an intermediate which may be the \( \eta^2 \)-bound alkyne complex of this mechanism. Knox previously proposed an alkyne insertion mechanism involving a radical intermediate; however, no experimental support was provided for this hypothesis.

![Figure 1.9: \([\text{CpFe}(\text{CO})(\mu-\text{CO})]_2\), HCC═CPh, and hv.](image)

Many two electron donors such as CO, CNCH\(_3\), phosphines, and phosphites form substitution products upon photolysis with \([\text{CpFe}(\text{CO})(\mu-\text{CO})]_2\). While phosphites form disubstituted complexes of \([\text{CpFe}(\text{CO})(\mu-\text{CO})]_2\) upon photolysis, such as \([\text{CpFe}(\mu-\text{CO})(\text{P(OMe)}_3)]_2\), phosphines only form monosubstituted complexes. Many alkynes, such as
Figure 1.10: The mechanism for phosphine and alkyne photosubstitution of $[\text{CpFe(CO)(μ-CO)}]_2$ proposed by Bursten, McKee and Platz.\textsuperscript{23}
phenylacetylene and dimethyl acetylenedicarboxylate, have formed photochemical insertion products of [CpFe(CO)(μ-CO)]₂ and other similar dinuclear species. The alkyne insertion products formed generally possess one of two structures, a dimetallacyclopentanone or a "flyover" type metallacyclobutenone (Figure 1.11).

![Figure 1.11: General structures of alkyne insertion products.](image)

The above series of reactions demonstrate not only the power of combining experimental techniques, such as laser flash photolysis and matrix isolation studies, to derive the intermediates involved in photochemical reactions, but also shows the usefulness of infrared spectroscopy to derive the structure of organometallic complexes. The structure of the intermediate, [CpFe]₂(μ-CO)₃, was based solely on the CO bands obtained by IR spectroscopy. The structure of the intermediate was crucial in deriving the proposed mechanism shown in Figure 1.10.
Much of the research presented in this dissertation will involve the use of IR spectroscopy to elucidate the structures of products. The CO stretching region of the infrared spectrum is 2400-1600 cm\(^{-1}\). The lower the CO stretching frequency, the weaker the C-O bond. Thus, estimations of the amount of metal backbonding to the \(\pi^*\) orbital of the CO bond, which consequently weaken the bond shifting the CO stretching band to lower energy, can be helpful in assigning structural characteristics of the species observed. Generally, IR bands for terminal CO ligands occur above 1850 cm\(^{-1}\) while those for bridging CO ligands occur between 1850 and 1750 cm\(^{-1}\).

The nature of bridging CO ligands can vary substantially in dinuclear complexes. Cotton suggested that bridging carbonyls cover a continuum of bonding interactions.\(^{30}\) This range includes CO ligands that are perpendicular to the M-M bonding axis (M-C-O \(\angle\) ca. 136°), to a linear semibridging CO with a M-C-O angle of 180°.\(^{31}\) The latter CO bridge is typically considered a four electron donor and CO ligands of this type exhibit unusually low stretching frequencies. Figure 1.12 shows the extreme cases of bridging discussed and an intermediate between the two, the bent semibridge. Because the position of CO stretching bands has
structural implications, infrared spectroscopy is a valuable tool in the study of organometallic complexes.

The types of techniques used to determine the photochemistry of \([\text{CpFe(CO)}(\mu-\text{CO})]_2\) have also been applied to a similar complex, \([\text{CpFe(CO)}]_2(\mu-\text{CO})(\mu-\text{CHCH}_3)\). This complex differs from \([\text{CpFe(CO)}(\mu-\text{CO})]_2\) only in one of the bridging ligands; one of the bridging CO ligands has been replaced by a bridging ethylidene ligand. This slight modification of the dinuclear framework has a profound effect on the resultant photochemistry. Although photolysis of \([\text{CpFe(CO)}]_2(\mu-\text{CO})(\mu-\text{CHCH}_3)\) in the presence of \(\text{CCl}_4\) still results in the formation of \(\text{CpFe(CO)}_2\text{Cl}\), no methylene containing products are detected. In addition, irradiation of \([\text{CpFe(CO)}]_2(\mu-\text{CO})(\mu-\text{CHCH}_3)\) with other dinuclear
transition metal complexes, such as Mn$_2$(CO)$_{10}$, does not result in the formation of crossover products. The crossover experiments suggest that no mononuclear radicals are formed, which in turn implies that the CpFe(CO)$_2$Cl complex does not form as a result of CpFe(CO)$_2^*$ but rather from a dinuclear intermediate. Indeed, LFP kinetic analysis shows the bimolecular rate constant for the reaction of [CpFe]$_2$(μ-CO)$_2$(μ-CHCH$_3$) with CCl$_4$ is 6.9 x 10$^3$ M$^{-1}$s$^{-1}$, which corresponds well to that for the reaction of [CpFe]$_2$(μ-CO)$_3$ with CCl$_4$, 4 x 10$^3$ M$^{-1}$s$^{-1}$. While LFP provides evidence of a long-lived species, no evidence of a short lived species is observed. Thus, the photochemical radical pathway of [CpFe(CO)]$_2$(μ-CO)(μ-CHCH$_3$) is effectively inhibited by the ethylidene bridge (Figure 1.13A).

As stated above, LFP demonstrates a long lived species. Matrix isolation IR spectra have also demonstrated evidence of CO loss (2132 cm$^{-1}$) and a triply-bridged structure, [CpFe]$_2$(μ-CO)$_2$(μ-CHCH$_3$) (1832 and 1795 cm$^{-1}$), similar to [CpFe]$_2$(μ-CO)$_3$, formed photochemically from [CpFe(CO)(μ-CO)]$_2$. The ethylidene bridge does not inhibit the CO-loss process (Figure 1.13B). Several other similar complexes, [CpFe(CO)]$_2$(μ-
Figure 1.13: Observed photochemical pathways of \([\text{CpFe(CO)}]_2(\mu-\text{CO})(\mu-\text{CHCH}_3)\).
CO\(_{(\mu-C(CN)SMe)}\) and \([\text{CpFe(CO)}]_2(\mu-\text{CO})(\mu-(E)-\text{CHCM}e=\text{CHCM}e)\), form CO-loss products upon irradiation as well.\(^{32}\) In addition, both \([\text{CpFe(CO)(p-CO)}]_2\) and \([\text{Cp}^*\text{Fe(CO)}]_2(\mu-\text{CO})(\mu-\text{CHCH}_3)\) undergo a double-CO-loss process (Figure 1.14).\(^{21,33}\)

Two electron donors such as phosphines, phosphites, and alkynes react readily with the CO-loss species, \([\text{CpFe}]_2(\mu-\text{CO})_2(\mu-\text{CHCH}_3)\), as expected (Figure 1.15).\(^{22,34}\) Of particular interest is the alkyne insertion reaction of \([\text{CpFe}]_2(\mu-\text{CO})_2(\mu-\text{CHCH}_3)\) with dimethyl acetylenedicarboxylate. Knox and coworkers report exclusive insertion into the hydrocarbyl carbon and metal atoms.\(^{26}\) There is no evidence of insertion into a carbonyl carbon and metal atom (Figure 1.16). The exclusive nature of the insertion suggests that some electronic differences between the methylene and CO groups favor methylene-alkyne interaction over carbonyl-alkyne interaction.

The difference between \([\text{CpFe(CO)(p-CO)}]_2\) and \([\text{CpFe(CO)}]_2(\mu-\text{CO})(\mu-\text{CHCH}_3)\), a mere carbonyl versus ethylidene bridge, results in similar yet different photochemical reactivities. Considering the methylene-bridged species of this study, \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) and \([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\), one would expect photochemical reactivities to be
Figure 1.14: Matrix photochemical and thermal reactions of [Cp*Fe(CO)]$_2$(μ-CO)(μ-CH$_2$) and [CpFe(CO)(μ-CO)]$_2$.\textsuperscript{21,33}
similar to those of \([\text{CpFe(CO)}]_2(\mu-\text{CO})(\mu-\text{CHCH}_3)\) in that all of the complexes have an alkylidene bridge. However, \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) and \([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\) only have a single bridge, a methylene bridge, and contain different metals. The different number and type of bridges and the different metals may play a role in altering the resultant photochemistry.

A single methylene bridge with no other bridging ligands is significant in that the 16 electron MLn fragments, \(\text{CpMn(CO)}_2\) and \(\text{CpCo(CO)}\), are isolobal with the \(\text{CH}_2\) fragment\(^{35}\). Therefore, the complexes are true dimetallacyclop propane s. Consequently, they may undergo the same photochemical reactions as cyclopropane. Photochemically, cyclopropane undergoes rearrangement to propylene, cis-trans isomerization, or methylene extrusion (Figure 1.17).\(^{36}\)
Figure 1.16: Photochemical alkyne insertion reaction of [CpFe(CO)]$_2$(μ-CO)(μ-CHCH$_3$).

where $R = \text{CO}_2\text{Me}$
Rearrangement to propylene involves the formation of a diradical.\textsuperscript{36a,36b,36c} It is conceivable that \([\text{CpFe(CO)}]_2(\mu-\text{CO})(\mu-\text{CHCH}_3)\) could form diradicals upon irradiation; however, the two bridges would be expected to maintain the metals in close proximity allowing immediate recombination. In the case of a single bridge, the single bridge could introduce enough flexibility to the framework allowing the two ML\(_n\) fragments to swing apart such that the lifetime of the diradical would increase. The lifetime of the singly bridged complex, \((\text{CO})_4\text{ReL}^\text{\dagger}\text{LRe(CO)}_4^\ast\) where \(L = \text{dppp}\), in decalin at 25°\text{C} is 36 ns.\textsuperscript{37} Poê and coworkers suggest that their kinetic results of the photofragmentation of \(\text{[Ru}_3(\text{CO})_{12}]\) do not discount the possibility of the formation of a short-lived diradical species.\textsuperscript{38} Further, Bryndza and Bergmen suggest a diradical
intermediate in the thermal formation of \([\text{CH}_3\text{Co(μ-CO)}_2(μ-\text{CpCH}_2\text{Cp})\text{Co(μ-CO)}_2(μ-\text{CpCH}_3\text{Cp})\text{Co(μ-CO)}_2(μ-\text{PPh}_3)]\). The lifetime may be too short to observe by LFP \(10^{-6}\) s; however, reactions with trapping agents such as CCl\(_4\) may allow for indirect evidence of the formation of a diradical species (Figure 1.18A).

Similarly, a 1, 3-diradical may form which is centered on the metal and hydrocarbyl bridged carbon atoms. This intermediate would be expected to immediately rearrange to form a terminal carbene complex (Figure 1.18B). This species is similar to the complex suspected in cis-trans isomerization of alkylidene-bridged complexes. A terminal carbene structure with terminal CO groups is free to rotate around the bond axis by 180° followed by reformation of the methylene bridge, resulting in cis-trans isomerization (Figure 3.53).

Another possibility upon photolysis is the photoejection of the methylene bridge. Presumably two ejected methylene groups could react to form ethylene. Although there are no examples of bridging alkylidene species extruding methylene groups, an Os dinuclear complex \((μ-(\text{C}_1,\text{C}_2)\text{CH}_2\text{CH}_2)\text{Os}_2(\text{CO})_6\) (Figure 1.19), photoejects its bridging ethylene.
Figure 1.18: Possible photochemical formation of 1, 3-diradicals of \([\text{CpCo(CO)}_2(\mu-\text{CH}_2)]\).
In the case of the molecules studied in this dissertation, the possible resulting species would be \([\text{CpMn(CO)}_2]_2\) and \([\text{CpCo(CO)}]_2\). The former is unknown while the latter has been characterized\(^{42,43,44,45}\). The existence of \([\text{CpCo(CO)}]_2\) suggests that methylene extrusion from \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) might result in an observable product, whereas methylene extrusion from \([\text{CpMn(CO)}_2]_2(\mu-\text{CH}_2)\) likely would result in decomposition products.

By analogy to \([\text{CpFe(CO)}]_2(\mu-\text{CO})(\mu-\text{CHCH}_3), [\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) and \([\text{CpMn(CO)}_2]_2(\mu-\text{CH}_2)\) would not be expected to undergo homolytic cleavage of the M-M bond to form mononuclear radicals. However, they would be expected to form CO-loss products upon irradiation. These products will likely maintain their methylene bridge due to the preference of methylene groups for a bridging rather than a terminal configuration.\(^3\)
In addition, the CO-loss products will probably exhibit a bridging CO due to the expectation that bridging CO groups tend to change ± 1 upon CO loss. This latter trend was exhibited in both \([\text{CpFe(CO)}(\mu\text{-CO})]_2\) and \([\text{CpFe(CO)}]_2(\mu\text{-CO})(\mu\text{-CHCH}_3)\) in which the respective CO-loss products are \([\text{CpFe}]_2(\mu\text{-CO})_3\) and \([\text{CpFe}]_2(\mu\text{-CO})_2(\mu\text{-CHCH}_3)\).

The complexes discussed above \([\text{CpFe(CO)}(\mu\text{-CO})]_2\), \([\text{CpFe(CO)}]_2(\mu\text{-CO})(\mu\text{-CHCH}_3)\), \([\text{CpCo(CO)}]_2(\mu\text{-CH}_2)\), and \([\text{CpMn(CO)}]_2(\mu\text{-CH}_2)\), demonstrate some possible ways to modify the dinuclear framework of dinuclear transition metal complexes. The type of metal atom, the type and number of bridging ligands, and the number of terminal ligands can all be changed within the constraints of the 18 electron rule. Each of these changes produces different complexes with different steric and electronic environments. As shown in the \([\text{CpFe(CO)}(\mu\text{-CO})]_2\) and \([\text{CpFe(CO)}]_2(\mu\text{-CO})(\mu\text{-CHCH}_3)\), these slight changes can have drastic effects on the photochemical reactivity of these seemingly similar complexes. The methylene-bridged complexes, \([\text{CpCo(CO)}]_2(\mu\text{-CH}_2)\) and \([\text{CpMn(CO)}]_2(\mu\text{-CH}_2)\), which contain a single bridging ligand, provide another opportunity to explore how these slight modifications can effect the observed photochemistry of this rich class of compounds. In addition to comparing their photochemical reactivities with previously studied double-bridged
systems, additional studies of the doubly-bridged complex, $[\text{Cp}^*\text{Fe(CO)}]_2(\mu\text{-CO})(\mu\text{-CH}_2)$, will also be undertaken.
Chapter II

Experimental

A. General Solution: Synthetic and Photochemical

All reactions and manipulations of air-sensitive compounds were carried out under an atmosphere of Ar or N₂ using standard procedures.⁴⁶ The N₂ (Matheson) and Ar (Linde) used were additionally purified by passage through consecutive columns containing activated De-Ox catalyst (Johnson and Matthey) and Drierite, respectively. Air-sensitive solids were handled and transferred in a Braun MB 150 M inert-atmosphere box equipped with a BASF R3-11 catalyst/Linde 13x molecular sieve system. Silica (Baker 60-100 mesh) and Alumina (Baker) were used as received unless stated otherwise. In particular, Alumina II was prepared by heating Alumina at 400°C under dynamic vaccum until no additional water was lost, producing Alumina I, followed by adding 3% by weight of water and shaking until uniform.⁴⁷
Large scale irradiations were performed in a 250-mL jacketed quartz photochemical reaction vessel. It consisted of a quartz immersion jacket containing a 450-W Hanovia medium pressure lamp, placed inside the reaction vessel. The immersion jacket was cooled by circulating tap water. A Teflon stopcock with a removable handle was used to enable the photochemical reaction vessel to sit centered on a stir plate. Figure 2.1 shows the typical photochemical reaction vessel setup. Solutions in this apparatus were both stirred and purged with Ar. Preparations of this nature were performed either in a large black reaction cabinet with butyl rubber vacuum tubing providing access to a Schlenk line or in a hood wrapped in Al foil.

Smaller scale reactions utilized a Pyrex Schlenk tube, a quartz photolysis tube with side arm (28 mm diameter by 150 mm length), or an NMR tube, either sealed by flame under vacuum or screw capped with a Teflon septum. While the Pyrex and quartz tube solutions were typically stirred or purged, the NMR tube solutions were not.

When using the reaction cabinet with the 450-W medium pressure Hanovia lamp, the immersion well was always placed ca. 15 cm from the solution. Here, the lamp immersion well and the solutions were often immersed in a water bath, cooled by the external circulation pump. With the water bath, temperatures ranged between 20 and 25°C. Whether a
Figure 2.1: Photochemical reactor.
water bath was used or not, the circulation pump removed heat from the reaction environment (Figure 2.2).

In contrast, for the reactions performed in the hood or on the optical bench where the 200-W Hg lamp (Oriel Corporation 66007 UNIV ARC medium pressure lamp with a research source f/1.0 UV grade fused silica lens and attached distilled water filter) was used, often no cooling of the sample was attempted. Sometimes cooled N\textsubscript{2} was blown on the experimental solution, either from evaporating liquid nitrogen (E-N\textsubscript{2}; Figure 2.3) or cylinder nitrogen gas cooled by liquid nitrogen (C-N\textsubscript{2}; Figure 2.3). Either way, the exact temperature of the solution during irradiation was not determined. The reaction vessels were placed between 28.5 and 34 cm from the distilled water filter of the lamp.

B. Reagents and Solvents

Most of the reagents to make the starting materials were purchased. Diazald (N-methyl-N-nitroso-p-toluenesulfonamide), sodium azide (NaN\textsubscript{3}), methyl phenyl sulfoxide (PhS(O)CH\textsubscript{3}), and trimethyloxonium tetrafluoroborate ((CH\textsubscript{3})\textsubscript{3}OBF\textsubscript{4}) were obtained and used as received from Aldrich. The diiodomethane reagents, CH\textsubscript{2}I\textsubscript{2} and CD\textsubscript{2}I\textsubscript{2}, were obtained from Aldrich and Cambridge Isotopes, respectively, and were rigorously purged before use. In contrast, (\textsuperscript{13}C)H\textsubscript{2}I\textsubscript{2} obtained from Isotec was
Figure 2.2: UV-Cabinet experimental setup.
Figure 2.3: E-N2 and C-N2 apparatuses for producing cool $N_2$. 
degassed via freeze-pump-thaw (FPT) before use. The NaH used was a 60% dispersion in mineral oil; however, it had previously been purchased and stored in the dry box. CpCo(CO)$_2$ and CpMn(CO)$_3$ were obtained from Strem and used as received. The method of Cirjak, Ginsburg, and Dahl$^{48 \text{a}}$ was used to prepare Na[CpCo(μ-CO)$_2$]$_2$ rather than the method reported by Schore, Ilenda, and Bergman.$^{48 \text{b}}$ For comparison purposes, CpCo(CO)$_2$I$_2$ was prepared from the method of King.$^{49}$ Both [CpFe(CO)(μ-CO)$_2$]$_2$ and [Cp*Fe(CO)]$_2$(μ-CO)(μ-CH$_2$) were prepared by Steve McKee and Yvonne Spooner, respectively, utilizing literature methods.$^{40,50,51}$ [Cp*Fe(CO)(μ-CO)$_2$]$_2$ was obtained from Strem.

Solvents were dried and degassed using standard methods.$^{52}$ Solvents were either freshly distilled or distilled into a solvent storage flask equipped with a Kontes valve and stored over molecular sieves. After drying over the appropriate drying agent, the solvents were used immediately if they were collected under Ar; however, if they were dried under air, they were either rigorously purged with Ar or degassed by the freeze-pump-thaw (FPT) method three times. The molecular sieves (Linde 5 Angstroms) were activated by heating under a dynamic vacuum at >250°C for several days until no additional water was removed. The molecular sieves were then stored in the dry box.
Tetrahydrofuran (Mallinckrodt Analytical Reagent), THF, was dried and distilled from potassium/benzophenone. Hexanes (Mallinckrodt Analytical Reagent), pentane (Spectrum Chemical), and petroleum ether (Mallinckrodt Analytic Reagent) were washed three times with concentrated sulfuric acid and subsequently washed with distilled water until neutral by Hydrion paper. These solvents were then predried over MgSO₄ and distilled over potassium metal. Methylene chloride (Mallinckrodt Analytical Reagent), carbon tetrachloride (Baker Analyzed Reagent), and acetonitrile (Mallinckrodt Analytic Reagent) were distilled over P₂O₅. Benzene (Baker Analyzed Reagent) and toluene (Mallinckrodt Spectroscopic Grade) were distilled over potassium/benzophenone and sodium metal, respectively. Ethylene glycol dimethyl ether (Aldrich), glyme, methylcyclohexane (Aldrich), and 3-methylpentane (Aldrich) were stirred over Na/K alloy for several days and vacuum transferred into a solvent storage flask, respectively, where they underwent three FPT cycles. Although spectroscopic grade cyclohexane (Aldrich) was degassed via three FPT cycles, it was not rigorously dried.

Diethyl ether (Mallinckrodt Analytical Reagent) was dried over strips of potassium metal and benzophenone in a solvent storage flask and vacuum transferred as needed. The potassium and benzophenone were loaded into the solvent storage flask in the dry box. Upon removal, the
solvent storage flask was evacuated and the Kontes valve sealed. Using a funnel, the ether was then added to the flask, carefully avoiding air to enter the flask. Once the flask was filled, it was shaken until the mixture became a dark blue.

Deuterated solvents were stirred over the appropriate drying agent, and vacuum transferred to a solvent storage flask with molecular sieves where they underwent three FPT cycles. These solvents were stored in the dry box. While CD$_3$CN, Cl$_2$D$_2$, and CDCl$_3$ (Cambridge Isotope Laboratories) were stirred over P$_2$O$_5$ for several days, C$_6$D$_6$ (Cambridge Isotope Laboratories) was stirred over Na/K alloy for several days. The deuterated THF was stirred over thin strips of potassium metal and benzophenone and vacuum transferred as needed. The deuterated methylcyclohexane (Cambridge Isotope Laboratories) was dried over molecular sieves for several days before it was vacuum transferred into a storage flask.

All liquid alkynes, phenylacetylene, diphenylacetylene, 1-hexyne, and dimethyl acetylenedicarboxylate (DMAD) were purchased from Aldrich and rigorously purged before use. Maleic anhydride was used as received from Spectrum Chemical. Both trimethylphosphine (1.0 M in toluene) and trimethylphosphite were obtained from Aldrich. The former was stored in the solvent storage flask equipped with a Kontes stopcock
while the latter was purged before each use. Triphenylphosphine was recrystallized from ethanol before use. Carbon tetrachloride was refluxed over $P_2O_5$ and stored over molecular sieves before use. The iodocarbons utilized, $\text{Cl}_4$ and $\text{CH}_2\text{I}_2$, were purchased from Aldrich. $\text{Cl}_4$ was used as received while $\text{CH}_2\text{I}_2$ was rigorously purged before use. Sublimation of the $\text{I}_2$ obtained from Mallinckrodt was necessary before use.

C. Instrumentation and Procedures

1. Infrared Spectroscopy

Either a Perkin Elmer FT-IR 1600 or, more recently, a Nicolet FT-IR Magna-550 infrared spectrometer was used for acquiring infrared spectra. Typical spectra were collected at 1 or 2 cm$^{-1}$ resolution and employing 24 or 32 scans. With the exception of the matrix isolation cell, the cell holder was placed so that the sample was located at the focal point of the instrument. A special cell holder was employed for use with the matrix cell, allowing the entire dewar to be lowered into the cell compartment through the window on top. The liquid cell used for routine solution samples consisted of 20 x 10 mm NaCl plates with a 0.2 mm Teflon spacer, LuerLock ports, and Teflon plugs. Solid infrared samples were either Nujol mulls or KBr pellets. The Nujol mull samples were run between two salt plates (NaCl, 30 mm) which were pressed together by
screwing together two SolvSeal connectors with o-rings. The SolvSeal connectors fit snugly in the solution cell holder. Figure 2.4 shows the make-up of this cell. KBr pellets were prepared either by a die press or a screw press. Both the solution and mull cells were stored in a desiccator between uses.

One of two methods of obtaining solution spectra were utilized. In the first method, a background spectrum of the empty cell was taken before each spectrum for both solvent and solution. This method required the solvent spectrum to be subtracted from the solution spectrum each time in the data work-up stage. More commonly, the solvent spectrum was obtained as a background spectrum. Consequently, the solution spectrum obtained as a sample spectrum was automatically ratioed to the solvent. Thus, no further subtraction was necessary.

While many solution samples were loaded in the glove box, others by necessity were prepared outside of it. In these cases, the infrared cell was purged with either N₂ or Ar and stoppered with its Teflon caps. A syringe, from which the needle had been removed, was used to obtain the sample for analysis. Just as the syringe neared the LuerLock connector, the stopper was removed and the syringe attached to it. Then the other cap was removed, the sample was added, and the caps were replaced.
Figure 2.4: Exploded view of mull IR cell.
2. Nuclear Magnetic Resonance (NMR) Spectroscopy

a) Solution

The NMR spectrometers utilized were a part of the Shared Analytical Instrumentation Laboratory (SAIL) of the chemistry department. Proton ($^1$H) spectra were obtained on the following self-run instruments: Bruker WP-200, AM-250, and MSL-300. Only the AM-250 and MSL-300 were used to obtain $^{13}$C spectra. The AM-250 spectrometer was also used in the acquisition of $^{31}$P spectra as well as low temperature $^1$H spectra. In addition, an operator-run AM-500 instrument was used for the acquisition of $^{13}$C and $^2$H spectra.

With the exception of $^2$H spectra, spectra for all nuclei were obtained in deuterated solvents. Residual proton resonances in deuterated solvents were used as internal standards for $^1$H and $^{13}$C spectra. Spectra of $^2$H were obtained in protonated pentane. A spectrum of protonated pentane with a drop of CD$_3$CN was first obtained. The peak positions of the $^2$H nuclei of pentane (natural abundance 0.015%)$^{53}$ were determined in reference to the residual $^1$H peak of CD$_3$CN (1.93 ppm). Hence, the $^2$H peak positions of the sample were set relative to the position of the $^2$H
peaks in pentane by setting the G value as determined relative to the residual protons in CD$_3$CN.

Either I-507-PP NMR tubes with caps and parafilm or Wilmad V-505 Screw cap NMR tubes were utilized. Air-sensitive samples were loaded with solvent in a glove box. Some samples were injected via syringe into an Ar filled screw cap tube through their replaceable septa. For samples that required flame sealing, an adapter was used to remove the loaded NMR tube from the glove box (Figure 2.5). Once removed from the box, the adapter was connected to a vacuum line via its 14/20 joint.

Figure 2.5: Adapter used for sealing NMR tubes.
The sample was frozen in a liquid nitrogen bath, a vacuum was pulled, and, using a gas/O₂ torch, the tube was sealed off and annealed. After annealing, the top part of the NMR tube was smeared with Apiezon wax to fill in any pinholes that might have been present.

Once the spectra were obtained, they were saved temporarily onto the given NMR computer. For long-term storage of spectra obtained on the AM-250 and MSL-300, these files were transferred first to a data station using a program called LIGHTNET. Next, the program NMRNET was used to transfer the data from the data station to a personal computer, which then allowed for the files to be saved onto 1.44 Mb floppy disks. A guide sheet outlining this procedure for saving files was developed and is shown in Appendix A.

b. Solid State

Solid state ²H NMR spectra were acquired by Pierre A. Florian by use of a Chemagnetics 9.4 Tesla NMR Spectrometer with a home built magic angle spinning (MAS) probe, spinning between 10 and 11 KHz. All spectra were referenced to CD₃CN.

The magic angle spinning (MAS) spectrum was acquired using a 1 pulse sequence with a 2 μs pulse width and a 5 s recycle delay. A total of 512 scans were acquired with a 500 KHz spectral width. The baseline of the MAS spectrum was interpolated manually to obtain a flat baseline.
A quadrupole echo sequence was used to acquire the static spectrum. Each of the two pulses was 2 μs in duration with a 10 s recycle time. The τ delay was 200 μs. A total of 3200 scans were acquired with a spectral width of 500 KHz.

3. UV-vis Spectroscopy

UV-vis spectra were obtained on an OLIS-upgraded Cary-171 instrument. Typical spectra were obtained using the low UV lamp setting and the adjustable IR source setting with the voltage at 60V. The number of data points were set such that there was a data point every 0.5 to 1 nm. While only 1 scan was obtained per spectrum, either 16 or 32 observations were taken per point. Spectra were typically obtained between 750 and 250 nm in hydrocarbon solvents such as toluene, cyclohexane, and 3-methylpentane. Quartz absorption cells were used with a pathlength of 1 cm.

In typical data collection, a spectrum of the solvent was first obtained, noting which face of the cell faced the source. This spectrum was saved and designated as the background. After the solvent was emptied from the cell, the solution was loaded into the same cell, and oriented in the instrument just as previously. The spectrum of the solution was then obtained and saved.
In the case of matrix isolation experiments, the spectra were obtained through the dewar. Thus, the cell in this case consisted of two CaF₂ plates with a 1 mm pathlength. Upon removing the cuvette holder from the sample compartment, the dewar holding stand from the optical bench was placed in the compartment. A grooved piece of metal attached to the bottom provided the guide to line up the holder, ensuring perpendicular positioning of the dewar and cell to the source. The metal rod that screws into the cuvette holder also screws into the side of the dewar holder. A piece of duct tape is wrapped around this rod on the outside of the instrument such that the placement of the rod with the duct tape flush with the outside of the instrument insured the cell was consistently placed the same distance from the sides of the sample compartment. Thus, the beam will impinge on the same location of the cell for each spectrum.

Before the dewar was placed in the sample compartment, the lights in the room were turned off and a vertical extender was added to the sample compartment. Once the dewar was carefully lowered into the compartment, a black cloth is wrapped over the top encircling the vacuum tubing extending out of the compartment. The cloth blocked any extraneous room light from the sample compartment. The actual spectra were obtained just as the cuvette spectra were obtained.
Because the OLIS software only allows for screen dumps, it was necessary to export the data to another program. The spectra were saved in the OLIS software as <filename>.dat files prior to exportation as <filename>.asc files. These files were then imported into either Deltagraph(PC) or Kaleidagraph(MAC) for subsequent work up.

4. Mass Spectroscopy

Fast atom bombardment (FAB) and electron ionization (EI) mass spectra were acquired by Mr. David C. Chang at the Ohio State Instrumentation Center, by use of a VG 70-250S mass spectrometer.

5. Electron Spin Resonance (ESR) Spectroscopy

A Bruker ER 300 Spectrometer with an ER 035M NMR Gaussmeter, a Hewlett-Packard 5352B microwave frequency counter, and a Bruker ER4111 VT continuous-flow LN$_2$ cryostat were used in the acquisition of the ESR spectrum. The instrument was operated by Craig F. Hemann and Dr. Russ Hille. The specific instrument parameter settings were 9.4584 GHz frequency, 100 KHz modular frequency, 10 G modular amplification and 12.2 mW power. All room temperature measurements were done with a standard flat-cell sample holder. The sample was continuously irradiated during spectral acquisition by a 200 W medium pressure Hg
lamp placed approximately 30 cm from the sample holder in the spectrometer cavity.

6. Laser Flash Photolysis Studies (LFP)

Kinetic data were obtained using a LFP apparatus (Figure 2.6). This apparatus consists of a Lumonics TE-861-4 excimer laser (351 nm, 60 mJ, 7 ns pulse width) or a Lambda Physik LPX-100 excimer laser (308 nm, 120 mJ, 10 ns pulse width). The excimer laser pulses irradiated the sample cell at a right angle to the 100 W Xe arc lamp monitoring beam. Both the laser beam and the monitoring beam were focused on the sample cell and the slit of the Oriel monochromator, respectively, using lenses. The monochromator was set for the wavelength to be followed. The front and back slits were both set at approximately 1 mm widths. An IP 28 photomultiplier tube was used to obtain signals. The signals were subsequently digitized by a Tektonix 7912 A/D transient digitizer. The system was controlled by an Apple Macintosh IIx computer.

Table 2.1: Excimer Laser Specifications.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Gas Mixture</th>
<th>Operating Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>351</td>
<td>He, F₂, Xe</td>
<td>60 mJ, 7 ns</td>
</tr>
<tr>
<td>308</td>
<td>He, HCl, Xe</td>
<td>120 mJ, 10 ns</td>
</tr>
</tbody>
</table>
Figure 2.6: Laser flash photolysis (LFP) and optical multichannel analyzer (OMA) apparatus.
Transient absorption spectra were acquired using an EG & G Princeton Applied Research model 1460 Optical Multichannel Analyzer (OMA). Both laser systems (351 and 308 nm) were used as excitation sources. Typical pulse widths were 800 or 900 ns. The sample cell was placed in the same position as for the kinetic studies; however, the lens focusing the monitoring beam onto the monochromator is slid back on the optical bench and the optic fiber cable from the spectrograph of the OMA is clamped flush with the exit slit of the sample cell holder. At 351 nm, signal averaging was usually necessary to acquire a spectrum with an acceptable noise level. This was done by collecting ca. 5 background (monitoring beam but no laser pulse) and ca. 5 active laser pulse signals in an alternating manner using the OMA. The background and active laser pulse signals were averaged, respectively. Finally, the spectrum was obtained by taking the log of the ratio of the average background pulse signal over the average laser signal. Because the 308 nm laser is more intense than the 351 nm laser, signal averaging was often not necessary.

D. Preparation of Starting Materials

1. Synthesis of [CpCo(CO)]_2(μ-CH_2)_5

a. Prepared in THF

A mixture of Na sand (0.609 g, 26.5 mmol) in 5 mL THF and a solution of CpCo(CO)_2 (4.010 g, 22.27 mmol) in 10 mL THF were cooled to
231 K by placement in an CH₃CN/CO₂ slush bath. The CpCo(CO)₂ solution was added to the stirring Na suspension via cannula. Immediately, a dark green solid formed signifying the formation of Na[CpCo(CO)]₂. This mixture stirred for one hour.

CH₂I₂ (2.1 mL, 26 mmol) was then added to the rigorously stirring mixture. At this time the flask was removed from the bath and allowed to warm to room temperature (ca. 40 minutes) after which, 20 mL of hexane was added causing formation of the white precipitate, NaI.

The flask was taken into the box for filtration. The solution was filtered through a 3 cm plug of Alumina II in a 60 mL sintered frit funnel and was washed with toluene until only a pale red filtrate emerged. After removal of the solvent by vacuum overnight and subsequent exchange of glyme with diethyl ether, the sample was left under dynamic vacuum overnight. This procedure resulted in an oil. The oil, dissolved in hexane, was added to an Alumina II column (1 cm x 17 cm) and eluted via hexane. Several bands emerged. Band A was yellow while Band B was dark red corresponding to the desired compound, [CpCo(CO)]₂(μ-CH₂). Removal of hexane from Band B resulted in a crystalline solid which was dissolved in 15 mL pentane, filtered, and placed in a CO₂/isopropyl alcohol (IPA) bath. Upon filtration and washing with a few mL of cold pentane, shiny, platelet
crystals were obtained. Yield, 0.4025 g, 11%. Spectroscopic Data: $^1$H NMR (benzene) $\delta$ 6.91, 4.64 ppm. IR (THF, cm$^{-1}$) 1996 (w) 1953 (s) 1918 (w). Literature: $^1$H NMR (benzene) $\delta$ 6.90, 4.64 (trans); 7.80, 6.22, 4.52 (cis) ppm. IR (THF, cm$^{-1}$) 1966 (w) 1957 (br s) 1924 (w).$^{5a}$

b. Prepared in Ethylene glycol dimethyl ether (Glyme)

Compound [CpCo(CO)]$_2$(μ-CH$_2$) was prepared as above using Na sand (0.604 g, 26.3 mmol) in 5 mL glyme, CpCo(CO)$_2$ (4.011 g, 22.28 mmol) in 10 mL glyme, and CH$_2$I$_2$ (2.1 mL, 26.2 mmol). This mixture was washed additional times with ether, but was not chromatographed on Alumina II beyond the initial filtration. The residue was washed (ca. 7 times) until the solvent pulled off by vacuum appeared only faintly yellow. Far less of this volatile material, CpCo(CO)$_2$, was noted in the glyme reaction compared to the THF reaction. The residue was dissolved in ca. 30 mL pentane, filtered and placed in a CO$_2$/IPA slush bath for recrystallization. The filtered recrystallization product was washed with ca. 5 mL cold pentane which resulted in a powder. This powder was pure by NMR but a small amount of insolubles were noted. Yield, 0.5494 g, 16%. Spectroscopic Data: Same as previous preparation.
c. Prepared with CD$_2$I$_2$ in Glyme

The preparation of [CpCo(CO)]$_2$(μ-CD) was performed precisely as described in 2-D.1.b using Na sand (0.650 g, 28.3 mmol) in 5 mL glyme, CpCo(CO)$_2$ (4.077 g, 22.64 mmol) in 10 mL glyme, and CD$_2$I$_2$ (7.080 g, 26.24 mmol). The residue was dissolved in 35 mL pentane, filtered and placed in a CO$_2$/IPA slush bath. Upon filtering and washing with cold pentane, shiny, platelets were obtained. The resulting crystals were pure by NMR and no insoluble material was noted. Yield, 0.7099 g, 20%.

Spectroscopic Data: $^2$H NMR (pentane) δ 6.94 ppm. $^1$H NMR (C$_6$D$_6$) δ 4.65 ppm. MS, m/e 320 M$^+$. Literature: $^1$H NMR (C$_6$D$_6$) δ 4.64 ppm. MS, m/e 320 M$^+$.5a

d. Prepared with (13C)H$_2$I$_2$ in THF

Due to the expensive nature of (13C)H$_2$I$_2$ this preparation started with Na[CpCo(CO)]$_2$ (0.0906g, 2.77 mmol) in 10 mL THF. To this stirred suspension (13C)H$_2$I$_2$ (0.5 g, 1.9 mmol) was added. After 30 minutes, 40 mL hexane was added. The mixture was filtered through a medium filter funnel and the solvent was removed via vacuum. The residue was chromatographed on Alumina II (1 cm x 21 cm) by hexane. The second band (dark red) may be eluted with toluene:hexane, although this sometimes speeds up its elution more than desired relative to the first
band. The dark red residue was dissolved in ca. 8 mL pentane, filtered and placed in a CO$_2$/IPA slush bath. Upon filtering and washing with 2 increments of ca. 2 mL cold pentane [CpCo(CO)]$_2$($\mu$-($^{13}$C)H$_2$) was obtained as shiny platelets. Yield, 0.1593 g, 26%. Spectroscopic Data: $^1$H NMR (C$_6$D$_6$) $\delta$ 7.20, 6.62, 4.65 ppm. $^{13}$C NMR (C$_6$D$_6$) $\delta$ 103.9(t). Literature: $^{13}$C NMR (C$_6$D$_6$) $\delta$ 207.8, 104.4, 86.5 (trans), 85.2 (cis).$^{5a}$

2. Preparation of [CpMn(CO)$_2$]$_2$($\mu$-CH$_2$)$_4$

a. Preparation of CpMn(CO)$_2$(THF)$^{54}$

A solution of CpMn(CO)$_3$ (1.005 g, 4.925 mmol) in ca. 200 mL of THF was transferred via cannulet into a 250-mL photoreactor equipped with a stir bar. While stirred and rigorously purged with Ar, the solution was irradiated for 2 1/4 hours with a 450-W Hanovia lamp in the photoreactor's immersion well. Although not used in this particular preparation, CpMn(CO)$_2$(THF) was also prepared using 350 nm bulbs in a Rayonet. An Ar-purged 500-mL THF solution of CpMn(CO)$_3$ (5.04 g, 24.7 mmol) in a 500-mL graduated cylinder equipped with a 24/40 ground glass joint was irradiated for 175 minutes in a walk-in refrigerator, yielding nearly complete conversion to CpMn(CO)$_2$(THF). Spectroscopic Data: IR (THF, cm$^{-1}$) 1929, 1851. Literature: IR (THF, cm$^{-1}$) 1925, 1850.$^{54}$
b. Preparation of \([\text{CpMn} \text{(CO)}_2]_2(\mu-\text{CH}_2)\) by Diazomethane Method

i. *Preparation of Diazomethane*\(^{55}\)

Diazomethane and \(\text{CpMn} \text{(CO)}_2\text{(THF)}\) were prepared simultaneously. In order to avoid \(\text{O}_2\) in the diazomethane prepared, the diazomethane kit (Aldrich; Z10, 025-0) equipped with a dropping funnel once assembled was purged with \(\text{Ar}\) for a minimum of one hour. Potassium hydroxide (1.8447 g, 32.879 mmol) and 3 mL distilled water were added to the 100 mL round bottom. Approximately 30 minutes were required for the KOH to completely dissolve. Next, 10 mL of 2-(2-ethoxy-ethoxy)ethanol and 6 mL ether were added. To an Ar-filled Schlenk flask, N-methyl-N-nitroso-\(p\)-toluenesulfonamide (Diazald) (3.6070 g, 16.836 mmol) and 30 mL purged ether were added. This Diazald solution was transferred to the dropping funnel. The apparatus was wrapped with glass wool, and a water bath was used to heat the KOH solution. As soon as ether began dripping into the collection flask,\(^{55c}\) the Diazald solution was added in a dropwise fashion to the KOH solution. Additional ether, ca. 8 mL, was added to the reaction mixture through the dropping funnel until the condensate dripped clear. The collection flask, a 100 mL air-less wear Schlenk flask, was removed under positive pressure, stoppered with a Teflon stopper, and placed in an salt/ice/water bath.
ii. Reaction of CpMn(CO)$_3$ and Diazomethane$^4$

The CpMn(CO)$_2$(THF) solution was transferred via cannulet or evacuated stiff Teflon tubing with attached needle through the stopcock of the photoreactor to a 3-neck flask attached to the Schlenk line. This solution was then cooled to -78°C and left open to Ar. The diazomethane solution was added dropwise via cannulet to the stirred CpMn(CO)$_2$(THF) solution. The reaction mixture was left overnight, allowing the slush bath to evaporate and the solution to warm to room temperature. The next morning the solvent was removed via vacuum leaving an oil residue.

In air, the oil was dissolved in toluene and filtered through a medium frit. The filtrate was transferred to a round bottom flask and the volume was reduced to ca. 3 mL on a rotary evaporator. This was added to a Silica/hexane column (Baker 60-200 mesh, 2 cm x 40 cm). The filtrate was first eluted with ca. 400 mL of hexane flashing with a positive Ar pressure. Next, it was eluted with ca. 200 mL of a 50/50 toluene/hexane solution. Finally, neat toluene was used. The second band (brown) was collected, evaporated to dryness, and placed on dynamic vacuum overnight. The residue was still an oil, but crystals of CpMn(CO)$_3$ were sublimed into the vacuum trap.
The residue was dissolved in ca. 20 mL pentane, filtered, and placed in the freezer. Upon cooling and filtering, brown-red crystals of \([\text{CpMn(CO)}_2(\mu-\text{CH}_2)]\) were obtained. Yield, 15.8 mg, 2%. Spectroscopic Data: \(^1\text{H NMR (C}_6\text{D}_6\) \(\delta 8.69, 4.14\) ppm. \(\text{IR (hexane, cm}^{-1}\) 1978 (w), 1937 (w), 1948 (vs), 1918 (s) 1902 (w). Literature: \(^1\text{H NMR (C}_6\text{D}_6\) \(\delta 8.65, 4.13\) ppm. \(\text{IR (hexane, cm}^{-1}\) 1978 (w), 1949 (vs), 1919 (s) 1902 (w).

c. Preparation of \([\text{CpMn(CO)}_2(\mu-\text{CH}_2)]\) by Sulfur Ylide Method\(^{56}\)

i. Preparation of S-methyl S-phenyl Sulfoximine, \([\text{PhS(O)(H)}\text{CH}_3]\)\(^{57}\)

In a 500-mL three-neck flask equipped with a mechanical stirrer, condenser, and dropping funnel, sodium azide (7.7161 g, 118.69 mmol), methyl phenyl sulfoxide (15.0365 g, 107.243 mmol), and 107 mL of undried chloroform were cooled in an ice bath. Concentrated sulfuric acid (27 mL) was added dropwise to the stirring solution over 25 minutes. Slowly, the ice bath was heated. At 20°C \(\text{N}_2\) began to evolve as evidenced through the mineral bubbler. The dropping funnel was replaced by a thermometer. The dropping funnel was replaced by a thermometer. When noticeable \(\text{N}_2\) evolution subsided, the water bath was switched with an oil bath and the temperature was stabilized at 40°C. After 12 hours, ice water (214 mL) was added causing the mixture to foam upon initial addition. After the salts dissolved, the aqueous and chloroform layers were separated. Salts were still present in the aqueous layer so another
40 mL water and 65 mL chloroform were added to the aqueous layer with subsequent separation. The aqueous layer was made slightly alkaline using almost 160 mL of a 20% NaOH solution, and was extracted twice with increments of 65 mL of chloroform. All the chloroform extractions were combined and dried for 1 1/2 hours over MgSO₄ followed by filtration. The solvent was removed at 42°C by evaporation. The resulting oil (12.3033 g) was found to be a 1:1 mixture of starting material, methyl phenyl sulfoxide, and product, s-methyl s-phenyl sulfoximine via NMR integration of their respective methyl group protons, 2.08 and 2.51 ppm in C₆D₆. The incomplete conversion was likely due to the a 5°C reduction from the literature temperature. Yield, 6.4642 g, 35%.

Spectroscopic Data: ¹H NMR (C₆D₆) δ 7.9 (m), 7.02 (m), 2.90 (s), 2.51 (s).

Literature: ¹H NMR (CDCl₃) δ 8.0-7.3 (two m), 3.45, 2.9 ppm.⁵⁷

ii. Preparation of (Dimethylamino)methylphenyloxosulfonium Fluoroborate, ([PhS+(O)N(HCH₃)CH₃]BF₄)⁵⁷

The method of Johnson, Haake, and Schroek⁵⁷ was followed precisely with the exception of starting with crude methyl phenyl sulfoxime (50% by mol). Thus, 10.0143 g of the crude mixture was used, which corresponds to 33.897 mmol of methyl phenyl sulfoximine and methyl phenyl sulfoxide, respectively. The methyl phenyl sulfoxide, which was filtered off during the crystallization, did not affect the reaction.
Yield, 6.0295 g, 66%. Spectroscopic Data: $^1$H NMR (C$_6$D$_6$) $\delta$ 8.23 (m), 7.86 (m), 4.02 (s), 3.16 (s) ppm. Literature: $^1$H NMR (CDCl$_3$) $\delta$ 8.2 (m), 3.95 (s), 3.1 (s) ppm.$^{57}$

iii. Preparation of (Dimethylamino)phenyloxosulfonium Methylide,\[(\text{Me}_2\text{N})(\text{Ph})\text{S(O)=CH}_2\] $^{57}$

The THF method described by Johnson, Haake, and Schroeck$^{57}$ was used. Sodium hydride (0.115 g, 4.79 mmol) was added to a solution of (dimethylamino)methylphenyloxosulfonium fluoroborate (1.2580 g, 4.6407 mmol) in 23.0 mL THF. After one hour, some of the fluoroborate salt remained in the bottom of the flask. Another equivalent of NaH was added, which was followed by the evolution of gas. After 30 minutes, solid remained in the flask but appeared to be unreacted NaH. This solution was used by carefully transferring the supernatant from the solid by cannulet. Because the experimental setup did not allow for the measurement of gas evolved, complete conversion was assumed, yielding a 0.2 M solution of the ylide product.

iv. Reaction of CpMn(CO)$_2$(THF) with (Me$_2$N)(Ph)S(O)=CH$_2$ $^{56}$

Two batches of CpMn(CO)$_2$(THF) (10.250 mmol) were prepared in succession and combined. The ylide (assumed 4.64 mmol) was prepared while the second batch of CpMn(CO)$_2$(THF) was photolyzed. With
vigorous stirring, the ylide solution was added to the solution of 
CpMn(CO)$_2$(THF). After following the reaction initially by IR, the mixture 
was left overnight. After a total of 8 hours reaction, the IR peak at 1851 
cm$^{-1}$, corresponding to CpMn(CO)$_2$(THF), was 1/5 its original height. The 
solvent was pulled off via vacuum and the residue was left under dynamic 
vacuum overnight. The residue was dissolved in ca. 6 mL toluene and 
chromatographed on a silica/hexane column (Baker 60-200 mesh, 2 cm x 
44.5 cm). Upon elution with ca. 500 mL petroleum ether, a yellow/green 
band emerged. A dark red band (green depending on light) was directly 
above the yellow band with no real separation. The mixture was next 
eluted with 9:1 petroleum ether/benzene. Fractions were collected starting 
after ca. 250 mL of the petroleum ether had eluted. The solvents were 
removed via vacuum. The fractions that were pure or virtually pure by 
NMR were combined and recrystallized in pentane at -26°C. Yield, 11.9 
mg, 0.6 %. Spectroscopic Data: Same as preparation with diazomethane 
above.
E. Reaction Chemistry of \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\)

1. Alkynes

a. Phenylacetylene

Phenylacetylene (4.0 mL, 6.0 x 10^{-5} \text{ mol}) was syringed into an NMR tube containing \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) (1.9 mg, 6.0 x 10^{-6} \text{ mol}) in 0.50 mL C_6D_6. This solution was cooled by E-N2 and placed 34 cm from the 200-W lamp filter. The solution was irradiated in four increments with NMR spectra taken at 5, 20, 50 and 70 minutes. The \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) peaks seemed to decrease while only a few small peaks appear in the methylene (ca. 8.4 ppm), cyclopentadienyl, and alkyl regions. In addition, the alkyl region peaks seem large compared to the new cyclopentadienyl region peaks.

Phenylacetylene (77 mL, 7.0 x 10^{-4} \text{ mol}) was added to the quartz tube containing \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) (0.1166 g, 3.665 x 10^{-4} \text{ mol}) in 25.0 mL toluene. The flask was immersed in a water bath. The solution was irradiated incrementally and was monitored by IR periodically. Spectra were obtained at 1, 3, 6, 9, and 11 hours of irradiation. Because little change in the IR was noted after 6 hours, another 4 equivalents of phenylacetylene (204 mL, 1.85 x 10^{-3} \text{ mol}) were added. At this point, a purple film above the solution was noted. After irradiation, no color
change had been noted. However, when the solution was transferred via cannulet to another flask, a green powder at the bottom of the tube was found. Spectroscopic Data: Listed in Table 2.2.

**Table 2.2: Spectroscopic Summary of Toluene Residue and Green Solid.**

<table>
<thead>
<tr>
<th></th>
<th>Observed (IR: cm⁻¹)</th>
<th>Observed (¹H NMR: ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>green solid IR(THF)</td>
<td>2021(w), 1995(w), 1953(s), 1819(m)</td>
<td></td>
</tr>
<tr>
<td>toluene residue IR(CH₂Cl₂)</td>
<td>2021, 1953, 1811</td>
<td></td>
</tr>
<tr>
<td>green solid NMR(C₆D₆)</td>
<td>7.89, 6.67, 4.95, 4.76, 4.48, 2.33, 1.96, 1.92, 7.8(m), 7.5(m)</td>
<td></td>
</tr>
<tr>
<td>toluene residue NMR(C₆D₆)</td>
<td>7.89, 5.67, 5.09, 4.95, 3.65, 2.33, 1.27, 7.8(m), 7.5(m)</td>
<td></td>
</tr>
</tbody>
</table>

b. Diphenylacetylene

Diphenylacetylene (6.6 mg, 3.7 x 10⁻⁵ mol) was added to an NMR tube containing [CpCo(CO)]₂(μ-CH₂) (1.4 mg, 4.4 x 10⁻⁶ mol) in 0.5 mL C₆D₆. This solution was placed 34 cm from the 200-W lamp filter. The solution was irradiated in three increments with NMR spectra taken at 0, 5, 15, and 80 minutes. The [CpCo(CO)]₂(μ-CH₂) peaks remained predominant while a few small peaks appear upfield of 4.64 ppm and, to a lesser extent, downfield of 7.5 ppm.
c. 1-hexyne

To the Pyrex tube containing \([\text{CpCo(CO)}]_2(\mu\text{-CH}_2)\) (7.3 mg, 2.3 x 10^{-5} mol) in 10 mL THF, 1-hexyne (1.3 mL, 1.7 x 10^{-2} M THF, 2.2 x 10^{-5} mol) was added via syringe. The solution was irradiated incrementally by the 450-W Hanovia lamp in the black box, taking IR spectra periodically. Spectra were obtained at 10, 30, 60, 145, and 215 minutes of irradiation. At 30 minutes of irradiation, the IR showed evidence for \([\text{CpCo(CO)}]_2(\mu\text{-CH}_2)\) and \(\text{CpCo(CO)}_2\), the 1953 cm^{-1} peak broadening and shifting to 1954 cm^{-1} and a peak growing in at 2021 cm^{-1}. At this point the irradiation compartment feels warm. As the irradiation continues, the solution takes on a murky appearance, suggesting decomposition.

d. Maleic Anhydride

A solution of maleic anhydride (10.0 mL, 5.2 x 10^{-2} M toluene, 5.2 x 10^{-7} mol) was syringed into an NMR tube containing \([\text{CpCo(CO)}]_2(\mu\text{-CH}_2)\) (1.4 mg, 4.4 x 10^{-6} mol) in 0.50 mL C_6D_6. Five minutes of irradiation by the 200-W lamp resulted in no apparent reaction visibly or by NMR. The solution was frozen in a CO_2/IPA slush bath overnight. Because 60 minutes of additional irradiation did not yield evidence of reaction via NMR, irradiation was then resumed with the 450-W Hanovia lamp in the reaction cabinet. After 125 minutes irradiation by the 450-W lamp, a very
fine precipitate was noted along with a decrease in starting material.
The growth of an IR band at 2021 cm\(^{-1}\) indicates the formation of a small amount of CpCo(CO)\(_2\).

e. Dimethyl Acetylenedicarboxylate (DMAD)

i. \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\)

In a typical NMR tube experiment utilizing the 200-W lamp on the optical bench, dimethyl acetylenedicarboxylate (0.50 mL, 7.0 x 10\(^{-3}\) M C\(_6\)D\(_6\), 3.5 x 10\(^{-6}\) mol) was syringed into an NMR tube containing \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) (1.1 mg, 3.5 x 10\(^{-6}\) mol). During each irradiation increment, the NMR tube, which was located 34 cm from the distilled water filter of the lamp, was inverted twice. The color change from red to an amber-brown followed the preferential growth of certain NMR peaks in the spectra obtained at 10, 20 and 30 minutes of irradiation.

Larger scale reactions were possible using a Schlenk tube. To the tube containing \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) (19.4 mg, 6.10 x 10\(^{-5}\) mol), DMAD (12 mL, 5.1 x 10\(^{-3}\) M toluene, 6.1 x 10\(^{-5}\) mol) was added. Positioned 28.5 cm from the distilled water filter of the 200-W Hg lamp, the solution was irradiated with aliquots removed periodically for NMR analysis. The spectra were taken at 1, 2, 3, and 3 3/4 hours. The last aliquot showed ca.
a 1:1 ratio between starting material and the predominant photoproduct. Solvent was removed via vacuum.

A Florisil (dried under dynamic vacuum at > 100°C) column was used to separate the predominant photoproduct from the other species present. The residue was dissolved in hexane and a few drops of THF. Half of this solution was added to a Florisil column (5 3/4" disposable pipet with glass wool plug, 5.1 cm Florisil, 0.2 cm sand, hexane). Elution with THF yielded a dark red band (BAND A). Once the eluent appeared clear, a green band (BAND B) was eluted with CH$_3$CN for ca. 5 minutes. In this time ca. 1/3 of the volume of a 4 dram vial was collected. Continuing to elute with CH$_3$CN, a yellow band was collected (BAND C). Spectroscopic Data: Fraction A, $^1$H NMR (C$_6$D$_6$) $\delta$ 10.85, 6.91, 4.77, 4.64, 4.51, 3.65, 3.62, 3.57, 3.41, 1.42, 0.61, 0.28 ppm. Fraction B, $^1$H NMR (C$_6$D$_6$) $\delta$ 8.78, 7.60, 4.74, 4.66, 3.68, 3.27, 1.38, 0.61. Fraction B, IR (THF, cm$^{-1}$): 1708(s), 1686(s), 1621(w). Mass Spectrum (HR-EI), m/e: 432 (M$^+$).

ii. [CpCo(CO)$_2$(i-CD$_2$)$_2$]

DMAD (7.4 mL, 6.2 x 10$^{-5}$ mol) in 12 mL C$_6$D$_6$ was placed in a Schlenk flask with [CpCo(CO)$_2$(μ-CD$_2$)$_2$] (19.8 mg, 6.19 x 10$^{-5}$ mol). The solution was purged with Ar in the hood while irradiated with the 200-W Hg lamp. NMR spectra were taken at 15 and 45 minute of irradiation. At
15 minutes the typically predominant species does not seem as preferentially formed. Spectroscopic Data: 45 Minutes, $^1$H NMR (C₆D₆) δ 8.78, 4.74, 4.67, 4.65, 3.68, 3.27 ppm among others.

Repeating the column procedure described earlier with a few minor changes proved to be insufficient to achieve comparable separation at this reaction scale. The residue was dissolved in hexane, a few drops of toluene, and a few drops of THF. The toluene had not been used previously, and it did not improve the procedure. This solution was placed on a Florisil column (5 3/4” disposable pipet, 5 cm Florisil, 0.2 cm sand, hexane) and eluted with THF. A dark red band immediately passed through (BAND A). The eluent never became colorless but rather appeared a constant light red color (BAND B). Because leaving the material on the column too long contributed to the formation of the white organic decomposition product, the solvent was switched to CH₃CN. Shortly thereafter, a red band eluted (Band C) that subsequently turned yellow (Band D) that consisted of ca. 1/2 the volume of a 4 dram vial. Finally, the still yellow eluent was collected (Band E). Data: Fraction A, $^2$H NMR (pentane) δ 6.94 ppm. Fraction C, $^2$H NMR (pentane) no signal. Fraction D, $^2$H NMR (pentane) δ 7.45 ppm.
Sublimation of the fractions containing insertion product and the organic product was conducted both with and without heating. A water cooled cold finger connected to a 100 mL round bottom flask via a 15 mm SolvSeal joint was used in both cases. First, half of the material was scraped into the round bottom flask, the latter was evacuated through a Kontes stopcock and then left under static vacuum. The flask was heated up to 43.2°C degrees and left with water flowing overnight. The organic compound sublimed, leaving a brownish solid on the bottom of the flask. The other half of the residue was treated identically with the exception of the absence of heating. Spectroscopic Data: With Heating, $^1$H NMR (C$_6$D$_6$) δ 0.28 (large grease), 1.40 (organic but much smaller), 3.27, 3.68, 4.67, 4.75, 8.77 (only hint of peak) ppm. Without Heating, $^1$H NMR (C$_6$D$_6$) δ 0.28 (large grease), 1.33(small), 3.24, 3.66, 4.64, 4.72 ppm. Organic Product, $^1$H NMR (C$_6$D$_6$) δ 1.34 ppm.

iii. [CpCo(CO)]$_2$(μ-^{13}CH$_2$)

Dimethyl acetylenedicarboxylate (0.5 mL, 1.0 x $10^{-2}$ M C$_6$D$_6$, 5.1 x $10^{-6}$ mol) was syringed into an NMR tube containing [CpCo(CO)]$_2$(μ-^{13}CH$_2$) (1.6 mg, 5.0 x $10^{-6}$ mol) in 0.5 mL C$_6$D$_6$. This tube was placed in a water bath in the reaction cabinet. The solution was irradiated with the 450-W Hanovia lamp where $^1$H NMR spectra taken at 0, 30, 90, 150 and 210
minutes while $^{13}$C NMR were only taken at 0, 30, and 90 minutes. By the end of irradiation, conversion of the starting material was nearly complete.

Simultaneously, an upscaled Ar-purged reaction with [CpCo(CO)]$_2(\mu-^{13}$CH$_2$) utilizing the quartz photolysis cell was performed in the reaction cabinet. After [CpCo(CO)]$_2(\mu-^{13}$CH$_2$) (19.8 mg, $6.21 \times 10^{-5}$ mol) was placed in the quartz photolysis cell, DMAD was added (10 mL, $6.2 \times 10^{-3}$ M C$_6$D$_6$, $6.2 \times 10^{-5}$ mol). Placing the solution in the same water bath as the NMR tube experiment, the solution was irradiated while purged with Ar.

As above, the irradiation increments were 30, 90, 150, and 210 minutes. However, although aliquots were removed at each interval, immediate $^1$H NMR spectra were only taken of the 30 and 90 minute increments while the 150 and 210 minute increment spectra were both obtained after the 210 minute increment was collected. Through 90 minutes of irradiation, the NMR spectra of the NMR tube experiment and quartz tube experiment indicated a similar ratio of [CpCo(CO)]$_2(\mu$-CH$_2$) to the preferentially formed product as indicated by representative peaks at 7.60, 4.74, 4.67, 3.68, and 3.27 ppm. The 150 and 210 minute increment $^1$H NMR spectra show no evidence for the preferentially formed product.
was found. This result is in contrast to the NMR tube experiment performed at the same time. Spectroscopic Data: 150 and 210 minute increments, \(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) absence of peaks at 7.60, 4.74, 4.67, 3.68, 3.27 ppm.

Solutions of the insertion product were prepared in pentane and hexane, solvents in which the compound was least soluble. The vials with caps were placed in the box freezer at -35°C. After a few weeks, the hexane vial produced a dark crystal which dissolved upon solvent warming.

2. Phosphorus Containing Compounds

a. Triphenylphosphine

*Dark Reaction* Triphenylphosphine (0.5 mL, 1.9 x 10\(^{-2}\) M C\(_6\)D\(_6\), 9.5 x 10\(^{-6}\) mol) was added to an NMR tube containing [CpCo(CO)]\(_2\)(μ-CH\(_2\)) (2.7 mg, 8.5 x 10\(^{-6}\) mol). NMR spectra were obtained after 40, 100, 160, and 220 minutes. No changes were noted except the disappearance of an impurity peak at 5.14 ppm after 100 minutes. No dark reaction was noted producing any new product peaks.

*Photochemical* After placing [CpCo(CO)]\(_2\)(μ-CH\(_2\)) (2.7 mg, 8.5 x 10\(^{-6}\) mol) in an NMR tube, triphenylphosphine (0.5 mL, 1.8 x 10\(^{-2}\) M C\(_6\)D\(_6\), 9.0 x 10\(^{-6}\) mol) was added. The tube was placed in the reaction cabinet with ice in
the circulating pump water bath. At time zero, no impurity peak at 5.14 ppm was noted. Spectra were obtained after 10, 20, and 30 minutes of irradiation. The spectra show that little [CpCo(CO)]2(μ-CH2) was consumed with an appearance of only small peaks in the baseline where the peak at 4.58 ppm is the largest. New spectroscopic peaks data: \(^1\)H NMR (C₆D₆) δ ca. 7.7, 4.58, 4.5, 4.45, 1.95 ppm.

This reaction was also followed by IR spectroscopy. A Pyrex Schlenk tube containing [CpCo(CO)]₂(μ-CH₂) (3.2 mg, 1.0 x 10⁻⁵ mol) in 5 mL toluene was placed 15 cm from the 450-W Hanovia lamp. Triphenylphosphine was added to this solution (1 mL, 1.7 x 10⁻² M toluene, 1.7 x 10⁻⁵ mol) via syringe. Aliquots for IR analysis were removed after 30, 60, and 90 minutes of irradiation. After 30 minutes, two peaks emerged while the [CpCo(CO)]₂(μ-CH₂) peak at 1953 cm⁻¹ decreased in intensity. No starting material was observed after 60 minutes. A color change to pale purple was noted after 90 minutes where all peaks decrease in intensity. The residue dissolved into a green C₆D₆ solution. Spectroscopic Data: IR (toluene, cm⁻¹) 30 minutes 2023, 1953, 1927; 60 minutes 2023, 1927; 90 minutes 2023 (vs), 1927 (vw). 90 minutes, \(^1\)H NMR (C₆D₆) δ 7.92, 7.31, 2.26 ppm.
A similar experiment utilized the quartz photolysis tube. In the tube, triphenylphosphine (1 mL, 1.7 x 10^{-2} M toluene, 1.7 x 10^{-5} mol) was added via syringe to [CpCo(CO)]_2(\mu-CH_2) (3.2 mg, 1.0 x 10^{-5} mol) in 5 mL toluene. Infrared spectra were obtained after 30, 45, and 60 minutes of irradiation. The trend was identical to that described above except that at 60 minutes the solution was green and no 2023 cm^{-1} peak was observed. Spectroscopic Data: IR (toluene, cm^{-1}) 30 minutes 2023(vw), 1953, 1927 (w); 45 minutes 1953, 1929 (w,b); 60 minutes 1928 (vw).

b. Trimethylphosphite

Dark Reaction To an NMR tube containing [CpCo(CO)]_2(\mu-CH_2) (2.1 mg, 6.6 x 10^{-6} mol) in 0.5 mL C_6D_6, trimethylphosphite (0.6 mL, 5 x 10^{-6} mol) was added via microliter syringe. Upon sitting in the dark for more than 17 minutes, no color change was observed. The ^1H NMR spectra showed a few small new peaks, but virtually no [CpCo(CO)]_2(\mu-CH_2) was consumed.

Photochemical Trimethylphosphite (0.6 \mu L, 5 x 10^{-6} mol) was added to an NMR tube containing [CpCo(CO)]_2(\mu-CH_2) (1.9 mg, 6.0 x 10^{-6} mol) in 0.5 mL of C_6D_6. This tube was irradiated in increments of 3, 6, 9, 13, and 17 minutes by a 200-W Hg lamp sitting 34 cm away. ^1H NMR spectra were taken at each increment along with a ^31P NMR spectra after 17 minutes of
irradiation. The solution turned amber colored or green depending on
the angle of light. Spectroscopic Data: 17 minutes, $^1$H NMR (C$_6$D$_6$) δ
4.88, 4.82, 4.75, 4.72, 4.64, 3.32, 3.38, 3.40, 3.42, 3.45, 3.49 ppm. 17
minutes, $^{31}$P NMR (C$_6$D$_6$) δ 173, 139.5 [P(OMe)$_3$], 30, 8.18 (strong), 2 ppm.

**Excess Trimethylphosphite** Using a microliter syringe, trimethylphosphite
(6.1 mL, 5.2 x 10$^{-5}$ mol) was added to an NMR tube containing
[CpCo(CO)$_2$(µ-CH$_2$)] (1.6 µL, 5.1 x 10$^{-6}$ mol) in 0.5 mL C$_6$D$_6$. Irradiation
with a 200-W Hg lamp in increments of 10, 15 and 20 minutes resulted in
reactivity. After 15 minutes irradiation, the solution was amber in color
and contained very little [CpCo(CO)$_2$(µ-CH$_2$)] via NMR. Spectroscopic
Data: $^1$H NMR (C$_6$D$_6$) δ 4.87, 4.75, 3.50, 3.45, 3.38, 3.33, 3.30, 3.25 ppm.
$^{31}$P NMR (C$_6$D$_6$) δ 139 [P(OMe)$_3$], 106, 30, 8.1, -42.3 ppm. Residue after
exposed to air, IR (hexane, cm$^{-1}$) 1965(m) and 1947(s).

c. Trimethylphosphine

**Dark Reaction** Trimethylphosphine (0.5 mL, 1.0 M toluene, 5.0 x 10$^{-4}$ mol)
was vacuum transferred into a Schlenk flask containing [CpCo(CO)$_2$(µ-
CH$_2$)] (3.4 mg, 1.1 x 10$^{-5}$ mol). The solution was wrapped with Al foil and
allowed to warm to room temperature. Within six hours the solution
changed from a red to yellow color. The solvent was removed via vacuum.
Spectroscopic Data: $^1$H (C$_6$D$_6$) δ 7.16, 4.65, 4.51, 2.11 (residual toluene), 0.9 (m), 0.77 (d, vs), 0.3 (s,s), 0.21 ppm. IR (hexane, cm$^{-1}$) 1930. Upon subsequent exposure to air, the solution changed from yellow to green.

3. Halocarbon Reagents

a. CCl$_4$

To a Pyrex Schlenk flask containing [CpCo(CO)$_2$(μ-CH$_2$)$_2$] (50.0 mg, $1.57 \times 10^{-4}$ mol), 40 mL of a 1% by volume CCl$_4$/THF solution was added via syringe. This flask was immersed in an ice bath and placed 15 cm from the 450-W Hanovia lamp. Throughout the experiment the temperature was maintained between 0 and 2°C. Stirring was attempted by using a magnetic air driven stirrer, but stirring stopped regularly during irradiation. The solution was irradiated for a total of 6 hours with aliquots removed every 30 minutes for IR analysis. After 240 minutes of irradiation, the solution appeared brownish whereas after 300 minutes of irradiation it looked green. The IR spectra showed a decrease in [CpCo(CO)$_2$(μ-CH$_2$)$_2$] as well as the growth of new peaks. Spectroscopic Data: 6 hours, IR (THF, cm$^{-1}$) 2131 (free CO), 2022 [CpCo(CO)$_2$], 1973 (vw), 1958 [CpCo(CO)$_2$].

Following the same reaction by NMR spectroscopy, CCl$_4$ (7.5 mL) was added to an NMR tube containing [CpCo(CO)$_2$(μ-CH$_2$)$_2$] (ca. 0.6 mg, 2 x
10^{-6} \text{ mol}) in ca. 0.75 mL CD_3CN. The tube was removed from the glove box and flame sealed under vacuum. The resultant 3 \times 10^{-3} \text{ M} solution was placed in an ice bath as above and irradiated with a 450-W Hanovia lamp for a total of 20 minutes. NMR spectra were acquired every five minutes. The peaks representing [CpCo(CO)]_2(\mu-\text{CH}_2) (6.67 and 4.96 ppm) were consumed while new peaks appeared. Interestingly, the peaks at 5.10 and 4.63 ppm grew initially upon photolysis, but then faded as irradiation continued. By 20 minutes of irradiation, the peaks of [CpCo(CO)]_2(\mu-\text{CH}_2) as well as peaks at 5.10 and 4.63 ppm are barely observable. Spectroscopic Data: $^1$H NMR (CD_3CN) δ (T = 0) 6.67, 5.63, 5.10, 4.96, 4.63, 2.53; (T = 5) 6.67, 5.54, 5.15, 5.10, 4.96, 4.63, 2.53; (T = 10, 15, 20) 6.67, 5.49, 5.15, 5.10, 4.98, 4.96, 4.92, 4.63, 2.53 ppm.

An IR experiment in which the temperature ranged from 15 to 24°C showed the formation of several transient peaks. Carbon tetrachloride (400 mL) was added to a Schlenk flask containing [CpCo(CO)]_2(\mu-\text{CH}_2) (51.3 mg, 1.61 \times 10^{-4} \text{ mol}) in 40 mL THF. The flask was placed in the reaction cabinet as above except that a water bath rather than an ice bath was used. The 4 \times 10^{-3} \text{ M} solution was irradiated for a total of 316 minutes while IR aliquots were removed at 15, 30, 45, 60, and 316 minutes irradiation. Not until 45 minutes of irradiation was any change at all
noted, at that time a very weak peak at 2020 cm\(^{-1}\) was noted. This peak grew slightly at 60 minutes irradiation. In contrast, after 316 minutes of irradiation, multiple new peaks were observed with consumption of \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\). This solution was immersed in a CO\(_2\)/IPA bath overnight. Upon warming the solution to room temperature and taking an IR a few of the peaks were no longer present. Spectroscopic Data: IR (THF, cm\(^{-1}\)) (T = 316 minutes) 2126, 2021, 1976, 1958, 1807, 1742 (residual water in atmosphere); T = next morning 2021, 1976, 1958, 1742. Part of this solution was exposed to air resulting in an immediate color change from green through blue-green to turquoise.

Another NMR tube experiment was performed where a less polar solvent was used, C\(_6\)D\(_6\). Carbon tetrachloride (3.4 mL, 5.4 x 10\(^{-3}\) mol) was added to an NMR tube containing \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) (1.0 mg, 3.5 x 10\(^{-6}\) mol) in 0.5 mL C\(_6\)D\(_6\). The solution was irradiated by a 200-W Hg lamp for a total of 6 minutes where NMR spectra were obtained at 0, 3, and 6 minutes irradiation. After 3 minutes a green precipitate was observed whereas after 6 minutes nearly complete consumption of \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) was noted. Spectroscopic Data: \(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) (3 minutes) 4.45, 4.41, 4.34; (6 minutes) ca. 4.41 ppm.
b. CI₄

*Dark Reaction*  Carbon tetraiodide (13.5 mg, 2.6 x 10⁻⁵ mol) in 5 mL THF was syringed into a Schlenk flask containing [CpCo(CO)]₂(μ-CH₂) (8.2 mg, 2.5 x 10⁻⁵ mol) in 20 mL THF. An IR spectrum obtained showed an immediate reaction. The residue was washed with hexane and filtered. Spectroscopic Data: IR (THF, cm⁻¹) (immediate) 2069, 2055 (sh), 2017, 1877; (34 minutes) 2069, 2055 (sh). ¹H NMR (C₆D₆) δ 4.27.

c. CH₂I₂

*Dark Reaction*  To an Al foil covered flask containing [CpCo(CO)]₂(μ-CH₂) (8.0 mg, 2.5 x 10⁻⁵ mol) in 20 mL THF, CH₂I₂ (5 mL, 4.8 x 10⁻³ M THF, 2.4 x 10⁻⁵ mol) was added. Infrared spectra were obtained at 5, 36, 100, 138, 142, and 245 minutes. No changes were observed other than a slight decrease in the [CpCo(CO)]₂(μ-CH₂) peaks.

Other experiments did show some reactivity in the dark. Diiodomethane (4.0 mL, 5.0 x 10⁻⁵ mol) was added to a Schlenk tube containing [CpCo(CO)]₂(μ-CH₂) (8.1 mg, 2.5 x 10⁻⁶ mol) in 10 mL THF. Aliquots were removed for IR analysis at 0, 30, 150 and 480 minutes. The formation and slight growth of a peak at 2021 cm⁻¹ with simultaneous decrease in the 1953 cm⁻¹ peak due to [CpCo(CO)]₂(μ-CH₂) were observed.
Similarly, NMR tube experiment gave evidence for some thermal reactivity. Deuterated THF (500 mL) was added to an Al foil covered NMR tube containing \([\text{CpCo(CO)}_2(\mu-\text{CH}_2)](3.7 \text{ mg, } 1.2 \times 10^{-5} \text{ mol})\). Diodomethane (2 \text{ µL, } 2.5 \times 10^{-5} \text{ mol}) was added to this solution. NMR spectra were obtained at 0, 20, 60, and 90 minutes. Spectroscopic Data: $^1\text{H NMR (d}_8\text{-THF)} \delta (T = 0) 6.67, 4.92, 2.42, 1.41; (T = 20, 60, 90 \text{ minutes}) 6.67, 5.13, 4.92, 1.41 \text{ ppm.}$

**Photochemical** To a Schlenk tube containing \([\text{CpCo(CO)}_2(\mu-\text{CH}_2)](4.7 \text{ mg, } 1.5 \times 10^{-5} \text{ mol})\) in 10 mL toluene, \text{CH}_2\text{I}_2 was added (0.8 mL, 1 mmol) in 50 mL toluene. Just before photolysis, the IR spectra showed slight reactivity with the emergence of a small peak at 2023 cm$^{-1}$. The solution was irradiated by the 450-W Hanovia lamp with IR aliquots removed after 10 and 30 minutes. New photochemical reactivity was observed. The solution appeared a murky purple after 30 minutes. Spectroscopic Data: IR (toluene, cm$^{-1}$) (10 minutes) 2065 and 2024; (30 minutes) 2069 and 1943 (toluene artifact).

Similar observations were made when comparing the irradiation of a quartz cuvette closed system to that of a Pyrex Schlenk tube open system. After 5 minutes of irradiation with the 450-W Hanovia lamp; neither solution had a noticeable color change. However, after 35 minutes
the quartz solution turned clear green \([\text{IR (THF, cm}^{-1}) \ 2069, 2022, 1957]\) while the Pyrex flask showed no apparent color change \([\text{IR (THF, cm}^{-1}) \ 2022, 1953]\). The Pyrex flask upon continued irradiation to 65 minutes continued the same trend with the peak at \(2021 \text{ cm}^{-1}\) growing while the \(1953 \text{ cm}^{-1}\) peak decreased in intensity and shifted to higher energy. The next 135 minutes of irradiation the Pyrex system was closed producing an olive green solution \([\text{IR (THF, cm}^{-1}) \ 2069, 2021, 1957]\). During that 135 minutes of irradiation of the Pyrex solution, the quartz cuvette had sat in the dark where the color changed to purple \([\text{IR (THF, cm}^{-1}) \ 2069]\). Upon sitting overnight the Pyrex solution turned purple \([\text{IR (THF, cm}^{-1}) \ 2069]\). Solvent was removed via vacuum. Spectroscopic Data: \(^1\text{H NMR (C}_6\text{D}_6\) \(\delta 4.33 \text{ ppm with other small peaks.}

d. \(\text{I}_2\)

**Dark Reaction** To an Al foil covered Schlenk flask containing \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) \((7.9 \text{ mg}, 2.5 \times 10^{-5} \text{ mol})\) in 20 mL THF, iodine \((5 \text{ mL,} 1.0 \times 10^{-2} \text{ M THF,} 5.0 \times 10^{-5} \text{ mol})\) was added. The solution immediately turned green. Reactivity was confirmed by an IR spectrum \([\text{IR (THF, cm}^{-1}) \ 2069, 2055(\text{sh}), 1875(\text{vw})]\). After 30 minutes the \(1875 \text{ cm}^{-1}\) peak was gone
leaving only the 2069 cm\(^{-1}\) peak. The solvent was removed via vacuum.

Spectroscopic Data: \(^1\)H NMR (CDCl\(_3\)) \(\delta 5.68, 2.62\) (broad, weak) ppm.

5. Other Metal Complexes

a. \([\text{CpFe(CO)(\text{\(\mu\)-CO})}]_2\)

Both \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) (1.4 mg, 4.4 \(\times 10^{-6}\) mol) and \([\text{CpFe(CO)(\(\mu\)-CO)}]_2\) (1.5 mg, 4.2 \(\times 10^{-6}\) mol) were added as solid to an NMR tube. The compounds were dissolved in 0.5 mL C\(_6\)D\(_6\). The solution was irradiated by the 200-W Hg lamp and \(^1\)H NMR spectra were obtained after 15, 35, and 50 minutes of irradiation. The solution was then frozen in liquid N\(_2\) overnight. Upon warming the next morning, the solution was irradiated for two additional 60 minute increments. Spectroscopic Data: \(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta 6.91, 4.64, 4.52, 4.41, 4.23\) ppm. IR (hexane, cm\(^{-1}\)) 1830.

F. Solution Reactions of \([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\)

1. \([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\) Only

*Room Temperature Photolysis* Using a 200-W Hg lamp, \([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\) (1 mM 90% MCH/10% 3MP) was irradiated. IR spectra were obtained at 5 and 12 minutes. The initial solution had sat in the dry box for several days [IR (90% MCH/10% 3MP, cm\(^{-1}\)) 2028(w), 1976(w), 1966(w), 1947(vs), 1917(s), 1900(w), 1883]. The peaks at 2028 and 1883 cm\(^{-1}\)
represent slight impurities. After 5 minutes of irradiation, the solution went from pale green to almost clear. The IR spectrum of the resultant solution was of poor quality but peaks could be distinguished [IR (90% MCH/10% 3MP, cm⁻¹) 2175 (broad, m), 2028 (m), 2017 (w), 1976 (w), 1967 (w), 1945 (s), 1929 (w), 1915 (w), 1882 (broad, w), ca. 1675 (vvs, probably artifact)]. After 12 minutes of irradiation, the peaks are the same but uniformly weaker.

Low Temperature Photolysis A small amount of [CpMn(CO)₂]₂(μ-CH₂) was dissolved in d₁₄-methylcyclohexane. The G value was set such that the farthest right peak of d₁₄-methylcyclohexane was located at 0.9 ppm. When this was adjusted, a room temperature (303 K) ¹H NMR spectrum was acquired [¹H NMR (C₆D₁₁CD₃) at 303 K 8.7, 4.57]. The temperature was lowered to 173 K at which a low temperature spectrum was obtained [¹H NMR (C₆D₁₁CD₃) at 173 K 8.63 with shoulder, 4.57(t)]. Immediately before placing the tube 30 cm from the 200-W Hg lamp, the solution was frozen in liquid N₂. The solution was irradiated for 5 minutes, inverting and refreezing once. The solution appeared red when frozen, but seemed to become paler as irradiation progressed. Immediately after irradiation, the NMR tube was placed in the spectrometer to begin the low temperature NMR process. The spectrum taken at 173 K indicated only
the presence of solvent, which was not as well defined as the earlier 173 K spectrum. The sample was warmed to 0°C in the instrument, upon removal a brown precipitate was observed.

Other low temperature NMR data were obtained on \([\text{CpMn(CO)}_2\text{(μ-CH}_2)]\) in CD\(_3\)CN. Spectroscopic Data: \(^1\text{H NMR (CD}_3\text{CN)}\) at 303 K δ 8.71, 4.69 ppm. \(^1\text{H NMR (CD}_3\text{CN)}\) at 250 K δ 8.60, 4.69 ppm.

Another attempt to irradiate while the solution of \([\text{CpMn(CO)}_2\text{(μ-CH}_2)]\) was frozen was performed in C\(_6\)D\(_6\). In an NMR tube, \([\text{CpMn(CO)}_2\text{(μ-CH}_2)]\) (1.0 mg, 2.7 × 10\(^{-6}\) mol) was dissolved in 0.5 mL of C\(_6\)D\(_6\). The NMR tube was flame sealed under vacuum, but an inferior adapter was used which may have allowed air and/or water into the tube when placing in on the vacuum line. The tube was cooled by CN\(_2\), causing water to condense on the tube. After irradiating the sample for 15 minutes, no color change was noted, but a white precipitate was observed. The NMR spectrum showed a peak at 0.4 ppm both before and after irradiation which suggests there was indeed water contamination. Spectroscopic Data: \(^1\text{H NMR (C}_6\text{D}_6)\) δ 8.69, 6.5, 6.28, 4.13, 3.88, 2.68, 0.4(water) ppm.
2. Dimethyl acetylenedicarboxylate (DMAD)

After placing [CpMn(CO)$_2$]$_2$(μ-CH$_2$) (0.8 mg, 2 x 10$^{-6}$ mol) into an NMR tube, DMAD (0.5 mL, 6.67 x 10$^{-3}$ M C$_6$D$_6$, 3 x 10$^{-6}$ mol) was added. The solution was irradiated with the 200-W Hg lamp for 10 minutes, inverting the tube at 5 minutes. After 10 minutes of irradiation, the solution appeared to have turned from green to yellow. When removed from the light, the solution appeared orange. During the NMR spectrum acquisition, a very fine orange precipitate settled to the bottom [${}^1$H NMR (C$_6$D$_6$) δ 5.15 ppm (very small)]. Extracting with CD$_3$CN, a yellow solution was obtained [${}^1$H NMR (CD$_3$CN) δ 4.68. IR (THF, cm$^{-1}$) 1979 (w), 1939 (s), 1909 (m), 1895 (sh), 1868 (w)]. Attempting to dissolve the orange solid in THF, a lightly colored solution was obtained [IR (THF, cm$^{-1}$) 2261 (m), 2113 (w), 1938 (w), 1909 (w), 1868 (w), 1738 (w, probably atmospheric water)]. Because both solutions were very dilute neither IR spectrum was clean.

G. Matrix Isolation Studies

1. Instrumentation and Apparatus

A SPECAC Model 21500 Variable Temperature Cell (Figure 2.7) and Controller (SPECAC, Inc., 301 Commerce Dr., Fairfield, CN 06430) were used. When the original thumb screws of the dewar became inoperable, the dewar was fitted with new washers and screws (Machine
The window material was CaF₂ for both the internal liquid cell and the outer windows of the vacuum dewar. Replacement variable temperature cell windows were ordered as needed (Spectral Systems, Inc, 35 Corporate Park Dr., Hopewell, Junction, NJ 12533). A lead spacer was placed between the internal cell windows producing a 1.0 mm pathlength in the cell. Evacuation of the dewar was necessary to maintain low temperature; for this purpose, a Leybold-Heraeus D4A Trivac direct drive pump with high vacuum tubing was used.

A 200 W medium pressure Hg lamp (Oriel Corporation 66007 UNIV ARC lamp with a research source f/10 UV grade fused silica lens) was utilized for irradiation. Because the lamp was equipped with a 1.5 inch liquid filter (distilled water), infrared wavelengths were removed from the light impinging on the sample cell. Specific wavelengths of light were also obtained by passing the light through filters of specific wavelengths. Although occasionally a 355 nm band pass filter (Oriel 51810) was used, use of broad band irradiation was typical. A laboratory jack was used to maintain the position of the lamp, and both the band pass filter holder and the dewar containing the cell were mounted on a 1.0 m low profile optical bench. The distance between the distilled water filter and the matrix dewar was between 28.5 and 40 cm.
Figure 2.7: Variable temperature IR cell (Specac 21500).
2. Experimental Procedure

A typical matrix experiment involved first taking a background spectrum of the empty cell in the dewar. The dewar itself could be lowered into the IR spectrometer and attached to a normal liquid cell holder. Once the background was obtained, the cell was removed from the dewar and taken into the dry box where it was filled with the solvent of choice for the experiment, typically 90% MCH/10% 3MP or neat 3MP. At this point the screws are carefully tightened to 3-pound inches using a MCX Torque Screwdriver (Seekonk Manufacturing Co., Inc., Perrin Ave., Seekonk, MA 02771) with an allen wrench adapter, tightening in 1/2 pound inch increments starting at 1 pound inch. The cell was placed in the dewar and another IR spectrum is obtained of the solvent only at 25°C (RTSOLV).

The vacuum hose was then attached to the dewar. The window warmer must be activated before cooling begins or water will likely condense on the outer window. Liquid N\textsubscript{2} was added to the coolant well of the dewar to cool to the experimental temperature. When the temperature reached ca. 8°C, the vacuum pump was turned on. Cooling slightly before turning on the pump decreased the amount of solvent lost to the vacuum. One cannot control the equilibration temperature of the cell, but the cell will equilibrate between 93 and 101 K where 95 K is the most common. This equilibration process typically took ca. 45 minutes. The cell was
considered equilibrated when the temperature remained constant for at least 10 minutes. Finally, a spectrum of the matrix material was obtained (LTSOLV). The liquid $N_2$ left in the coolant well was removed and the cell was allowed to warm to room temperature. Once the cell reached ambient temperature, it was removed from the dewar and the solvent was removed.

Solutions prepared with stock solvent or solvent mixture and the compound to be studied were prepared in the dry box. The above procedure was repeated, loading the solution in the cell inside the box. Using the empty cell as the IR spectral background, a room temperature solution spectrum was acquired (RTSOLN). Cooling as above, a low temperature solution spectrum was obtained (LTSOLN). Typically, the cell will drop to the same temperature for both the solvent and solution on a given day, although on occasion the temperature will vary by a few degrees.

The above RTSOLN and LTSOLN spectra do not contain obvious useful information in their initial form. The solvent only spectra must be subtracted from them to obtain informative solution spectra. Thus, LTSOLN minus LTSOLV results in a solution spectrum of the compound at low temperature without solvent peaks complicating its interpretation (Figure 2.8). The same procedure is performed for all spectra.
Figure 2.8: Obtaining an IR spectrum of \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) after 300 s of irradiation at 96 K in 3MP. (a) Raw data spectrum after 300 s of irradiation (b) Raw data spectrum before irradiation (c) Resultant spectrum (Spectrum a - Spectrum b).
Once the before-irradiation spectra were obtained, irradiation began. The lamp required ca. 30 minutes to warm up so usually it was turned on early with the placement of a piece of Al foil or a black cloth over the distilled water filter. Once irradiation began, care was taken to ensure the lamp was at the proper height and that the lamp was focused (handle on distilled water filter) on the sample cell. The sample was irradiated for the desired time increments with IR spectra obtained at the chosen intervals. The dewar well was replenished often during the irradiation period. As before, to obtain solution spectra at the irradiation intervals, the low temperature solvent-only spectrum was subtracted from them.

Another way to view the spectra is to create difference spectra. By subtracting the before irradiation spectrum (LTSOLN) from the after irradiation solution spectrum (hvSOLN), a difference spectrum was created which showed the changes occurring during the time between the spectra. In these cases consumed species peaks appear negative while produced species peaks appear positive (Figure 2.9).

Finally, the cell was allowed to warm to room temperature, at which point another room temperature spectrum was acquired. This procedure allowed one to observe whether the photoproducts are stable to room temperature.
Figure 2.9: Creation of a difference IR spectrum of 
\([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) after 300 s of irradiation at 96 K in 3MP. (a) Spectrum after irradiation (b) Spectrum before irradiation (c) Difference spectrum (Spectrum a - Spectrum b).
3. Variations in Procedure

Thermal Reactions  Once photoproducts were formed it was useful to see if they were reactive even at low temperatures. Thus, by allowing the cell to sit at low temperature in the dark, one can then obtain a difference spectrum showing the changes occurring at that particular temperature in the dark. This is achieved by subtracting the spectrum obtained at the beginning of the dark period from the spectrum acquired at the end of the dark period.

Annealing  Often it is useful to “anneal” the matrix after irradiation of the solution has begun. In the “annealing” process, the cell warmer was turned on and liquid N\textsubscript{2} was removed from the coolant well while irradiation was continued. Typically, the cell was allowed to warm to a specific temperature, 150 K for example. Once at the target temperature, the cell warmer was turned off, liquid N\textsubscript{2} was added to the well, and the cell was cooled back down to the original temperature where an IR spectrum was obtained.

UV-vis  The UV-vis spectra of the resultant photoproducts were also obtainable. After a given IR spectrum was taken, the dewar was placed into the Olis-upgraded Cary-17I sample compartment for acquisition of a spectrum. The IR spectrum provided the spectroscopic handle on what species were present in the matrix when the UV-vis spectrum was
obtained. The details of how these spectra were obtained is in section 2-C.3.

**H. Laser Flash Photolysis (LFP) Studies**

The following compounds, $[\text{CpCo(CO)}]_2(\mu-\text{CH}_2)$, $[\text{CpMn(CO)}]_2(\mu-\text{CH}_2)$, $[\text{CpFe(CO)(\mu-CO)}]_2$, were recrystallized from the suitable solvents before use, while $[\text{Cp*Fe(CO)(\mu-CO)}]_2$ was used as received. The $[\text{Cp*Fe(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)$ obtained from column chromatography was sufficiently pure (via NMR) and used as prepared. The Co and Mn dimers were stored under an inert atmosphere until use.

All solutions were prepared under an Ar atmosphere in a dry box. The concentration of LFP samples was such that the dimer had an absorbance of 1 at 351 nm except where stated otherwise. The concentration necessary varied depending on the dimer, but was between $(1.4 \text{ and } 1.9) \times 10^{-4}$ M. Serial dilutions were performed to obtain the desired concentrations. The compounds were weighed on an analytical balance (0.0001 g) under air and transferred to a dry box for subsequent solution preparation. Solvents used in these studies included spectroscopic grade toluene and cyclohexane, 3MP, and MCH. With the exception of cyclohexane, all solvents were rigorously dried and degassed
(FPT). Cyclohexane was degassed upon receipt, but was not rigorously
dried; thus, the cyclohexane did contain water.

The 1 cm square quartz cells used were either a homemade suprasil
quartz cell or a fluorescence cell. The former was sealed with a septum
while the later was sealed with a 9 mm solvseal cap. Where quenching
agents (purged with Ar) were employed the cell was charged with 1.4 mL
of stock dimer solution, a certain amount of quencher and sufficient
solvent to give a total volume of 2.0 mL in each cuvette. The samples were
then removed from the box for immediate LFP analysis.

The experimental procedure involving the reaction of the CO-loss
intermediates with CO was slightly modified from the description above.
Here, 2.0 mL of stock solution was added to the fluorescence cell and
capped with a 9 mm solvseal adapter which allowed for a septum. Outside
the box, the solution was purged with CO gas for 5 minutes to saturate the
solution before flashing although 2 minutes would have been sufficient.59
Because this experiment was done in cyclohexane, water was present as
well. However, only a maximum of 4 mM60 of water was present versus
13.5 mM CO.61 Thus, the expectation is that the qualitative number
obtained is representative of the reaction of the CO-loss intermediate with
CO.
The reaction kinetics of the dinuclear intermediate and quencher in toluene as well as the dinuclear intermediate and CO in cyclohexane were pseudo-first-order with respect to the concentration of the quencher for the former and of CO in the latter. Thus, the processes can be described by Equation 2.1 where $k_{obs}$ is the observed pseudo-first-order decay rate constant, $k_0$ is the sum of the first order and pseudo-first-order rate constants for all intermediate processes that do not involve the quencher and $k_q$ is the second-order rate constant for the reaction of the intermediate and quencher. By measuring the value of $k_{obs}$ as a function of quencher concentration, the plot of $k_{obs}$ verses [quencher] yields a linear plot where the slope is equal to $k_q$ in units of $M^{-1}s^{-1}$. For the reaction of the CO-loss intermediate with CO, the second-order-rate constant was obtained by dividing the observed rate constant by the [CO], 13.5 mM.61

The data were imported into Kaleidagraph on a Macintosh IIcx computer. The initial data points up to just after the resultant bleaching points were removed. Thus, a true zero point was obtained at the laser flash. The simple pseudo-first-order kinetic analysis equation is shown in Equation 2.2 while Equation 2.3, an exponential expression, was used

\[-k_{obs}t = \ln((A_t - A_0)/(A_0 - A_\infty))\]  

(2.2)
\[ y = \frac{a_0}{(1 + ka_0t)} + a_\infty \] (2.3)

to evaluate these systems: \( y \) is \( \Delta A \), \( t \) is the time from the flash, and \( a_\infty \) is \( \Delta A \) at \( t_\infty \). If \( a_\infty \) went to zero at \( t_\infty \), then \( a_0 \) would equal \( y \) at \( t_0 \). However, \( a_\infty \) is some number at \( t_\infty \) rather than zero, so \( a_0 \) is defined as the difference between \( y \) at \( t_0 \) and \( y \) at \( t_\infty \). Because concentration is directly proportional to absorbance, Equation 2.3 yields information about the concentrations. However, because the value of absorbance obtained in our experimental setup is proportional to the voltages applied to the PMT,\(^6\) only values obtained in the same experimental run can be averaged for analysis.

Because \( \Delta A \) was followed at a wavelength where the CO-loss species absorbs more strongly than the original dimer, a decay is followed. The complexes, \([Cp^*Fe(CO)]_2(\mu-CO)(\mu-CH_2)\), \([CpFe(CO)(\mu-CO)]_2\), and \([CpCo(CO)]_2(\mu-CH_2)\), were followed at 490, 515, and 550 nm, respectively.

The data obtained in these studies should be viewed in a qualitative rather than quantitative manner. As previously mentioned, the total time the instrument can follow is 20 \( \mu s \), but the actual time followed is even less, and the results are, consequently, not very reliable. Thus, for the systems without quencher where the half-lives are on the order of 3s,\(^{14,15a,16}\) much less than 1 half-life was followed. Five data sets (1 laser
flash each) were obtained for a given sample for each concentration. These data sets were averaged before analysis by equation 3 yielding a single \( k_{\text{obs}} \) value.

Even with quencher added only two systems studied, P(OMe)\(_3\) and PMe\(_3\) added to \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\), manifested half-lives (2 \( \mu \text{s} \)) of such an order or magnitude that multiple half-lives could be followed. Those quencher studies are based on one or two laser shots (data sets) on a single sample. Unfortunately, few quencher concentrations were available for the \( k_{\text{obs}} \) verses [quencher] plots for the determination of \( k_Q \). Therefore, the values of \( k_Q \) reported should be viewed in terms of trends rather than absolute values.

For data analysis, the values of \( k_{\text{obs}} \) having correlation coefficients greater than 0.78 were used. Where multiple \( k_{\text{obs}} \) values were obtained, they were used for plots of second-order rate constants.

A few experiments were designed such that only a very short time (2 \( \mu \text{s} \)) was followed. Although these were not amenable to kinetic analysis, even for qualitative results, the shape of their absorption profiles provided information about the photochemical processes occurring, which will be discussed later. These were the only experiments which used a 308 nm
laser flash and dimer concentrations to give and absorbance of 1 at 308 nm.

All data were obtained at ambient laboratory temperature. The rate constants are shown in Table 2.3, Table 2.4, and Table 2.5.

Table 2.3: Pseudo-first-order Rate Constants from the LFP Kinetic Data for the Reaction of \([\text{Cp}^*\text{Fe(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) with CO in Cyclohexane (\(\lambda_{\text{obs}} = 490 \text{ nm}\)) and Calculated \(k_Q\).\(^a\)

<table>
<thead>
<tr>
<th>[CO] (mM)(^61)</th>
<th>(k_{\text{obs}} (s^{-1}))</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.5</td>
<td>((1.50 \pm 0.07) \times 10^5)</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>(k_Q = 1 \times 10^7 \text{ M}^{-1} \text{s}^{-1})</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) [dimer], \(1.4 \times 10^{-4} \text{ M}\), closer to \(A_{308} = 1\) with 351 nm flash

Table 2.4: Pseudo-first-order Rate Constants from the LFP Kinetic Data for the Reaction of \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) with \(\text{P(OMe)}_3\) in Cyclohexane (\(\lambda_{\text{obs}} = 550 \text{ nm}\)) and Calculated \(k_Q\).

<table>
<thead>
<tr>
<th>[P(OMe)(_3)] (M)</th>
<th>(k_{\text{obs}} (s^{-1}))</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>((2.00 \pm 0.08) \times 10^2)</td>
<td>0.78</td>
</tr>
<tr>
<td>1.27</td>
<td>((2.56 \pm 0.03) \times 10^6)</td>
<td>0.99</td>
</tr>
<tr>
<td>2.54</td>
<td>((6.76 \pm 0.09) \times 10^5)</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>(k_Q = 1 \times 10^6 \text{ M}^{-1} \text{s}^{-1})</td>
<td>0.96</td>
</tr>
</tbody>
</table>
Table 2.5: Pseudo-first-order Rate Constants from the LFP Kinetic Data for the Reaction of $[\text{CpCo(CO)}]_2(\mu$-$\text{CH}_2)$ with PMe$_3$ in Cyclohexane ($\lambda_{obs} = 550$ nm) and Calculated $k_Q$.

<table>
<thead>
<tr>
<th>[PMe$_3$] (M)</th>
<th>$k_{obs}$ (s$^{-1}$)</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$(2.00 \pm 0.08) \times 10^2$</td>
<td>0.78</td>
</tr>
<tr>
<td>0.15</td>
<td>$(5.94 \pm 0.04) \times 10^5$</td>
<td>0.99</td>
</tr>
</tbody>
</table>

$k_Q = 4 \times 10^6$ M$^{-1}$s$^{-1}$ 1
Chapter III

Results and Discussion

The photochemistry of dinuclear cyclopentadienyl transition-metal complexes was discussed in the introduction. In this dissertation, the photochemical reactivity of \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\), \([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\), and, to a lesser extent, \([\text{Cp*Fe(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\), will be explored. Both \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) and \([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\) are expected to undergo CO loss upon irradiation while \([\text{Cp*Fe(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) has already demonstrated CO-loss reactivity upon irradiation.\textsuperscript{33} Photochemical radical formation will also be probed in these complexes by transient absorption spectroscopy and reactivity studies. Comparison of the photochemical reactivity of these complexes to previously studied complexes, such as \([\text{CpFe(CO)}](\mu-\text{CO})_2\) and \([\text{CpFe(CO)}]_2(\mu-\text{CO})(\mu-\text{CHCH}_3)\), provide additional data with regard to the photochemical tunability of dinuclear organometallic complexes.
The initial dinuclear methylene-bridge transition-metal complexes chosen for this study, [CpCo(CO)]$_2$(μ-CH$_2$) and [CpMn(CO)$_2$]$_2$(μ-CH$_2$), were in part chosen for two practical reasons, namely the existence of established synthetic routes coupled with the inexpensive nature of the starting materials used in these syntheses. The Theopold and Bergman$^5$ preparation of [CpCo(CO)]$_2$(μ-CH$_2$) proved easy to follow with acceptable yields, but difficult to upscale efficiently. On the other hand, the synthesis of [CpMn(CO)$_2$]$_2$(μ-CH$_2$) proved difficult. At first only NMR evidence was found with no isolable product. Thus, before the study of the photochemistry of these molecules could occur in earnest, a study of the optimization of their preparations ensued.

**Increasing the Amount of Isolated [CpCo(CO)]$_2$(μ-CH$_2$)**

Theopold and Bergman$^5$ report a 48% yield in the preparation of [CpCo(CO)]$_2$(μ-CH$_2$). However, by this method the best yield attained here was 26%. Upscaling this preparation proved cumbersome resulting in an even lower yield. The issue, however, was not the yield, but the overall amount of [CpCo(CO)]$_2$(μ-CH$_2$) isolated for additional reactivity studies.

Bypassing the time-consuming isolation of the intermediate compound, seemed plausible based on the preparation of CpCo(μ-CO)$_2$(μ-CH$_2$CH$_3$CH$_2$)CoCp. Here, Theopold and Bergman formed Na[CpCo(μ-
CO)]₂ in glyme in situ at -40°C. 1,3-diiodopropane was added to produce the propanated compound, CpCo(μ-CO)₂(μ-CH₂CH₃CH₂)CoCp, with a 33% yield after a relatively simple chromatography procedure and wash.⁶³ Because of the opportunities to start with a much larger amount of CpCo(CO)₂, even with a lowering of the yield, more product seemed likely to be isolated. The modified preparation scheme is shown in Figure 3.1.

Following this plan, up to about 5 times the typical amount of [CpCo(CO)]₂(μ-CH₂) was isolated than when the original preparation was followed. A comparison study was also done between using glyme and THF as the solvent. While both are ethers and have similar solvent qualities, glyme is more difficult to dry and to remove via vacuum than THF. Thus, it appeared reasonable to use THF, which is easier to manipulate instead of glyme. While the yields obtained were similar, 10-15%, there appeared to be more unreacted CpCo(CO)₂ in the THF reaction, as noted by the large amount of a red/yellow volatile substance removed with the solvent and a less viscous resultant oil. Thus, the conversion to the intermediate compound, Na[CpCo(μ-CO)]₂⁺, appears to be more complete in glyme.
Figure 3.1: Preparation scheme of \([\text{CpCo(CO)}_2(\mu-\text{CH}_2)]\).
In the original \(\text{CpCo(\mu-CO)}_2(\mu-\text{CH}_2\text{CH}_3\text{CH}_2)\text{Cp} \) preparation, the authors only perform a filtration through a 3 cm plug of Alumina II, the Alumina was washed with toluene until the washings were no longer dark green in color, followed by a pentane wash.\(^{63}\) With the exception of the pentane wash, the same work-up procedure was used in the \(\text{[CpCo(CO)]}_2(\mu-\text{CH}_2)\) preparation. After filtering the reaction mixture through Alumina II, the column was washed with toluene until the washings were no longer dark red, the color of \(\text{[CpCo(CO)]}_2(\mu-\text{CH}_2)\). Recrystallization with pentane resulted in either analytically pure product or product with a small amount of insoluble material. However, if an additional column (Alumina II, 1 x 21 cm) is run with elution by either hexane or hexane/toluene followed by recrystallization, analytically pure product is isolated. The extra column appears to lower the yield by about 5%, but the purity of the product is more important than the yield. Thus, the best procedure presently for preparing \(\text{[CpCo(CO)]}_2(\mu-\text{CH}_2)\) on the 500 mg scale involves using glyme as the solvent, filtering through a 3 cm frit to remove reaction solids and unreacted Na, chromatographing on a 1 x 20 cm column, and finally recrystallizing in pentane. This is described in detail in section 2-D.1c.
Increasing the Yield of \([\text{CpMn(CO)}_2\text{]}_2(\mu-\text{CH}_2)\)

The original preparation reported consists of three individual steps:

the formation of \(\text{CpMn(CO)}_2(\text{THF})\), Figure 3.2a, the formation of \(\text{CH}_2\text{N}_2\), Figure 3.2b, and the facile low temperature reaction of \(\text{CpMn(CO)}_2(\text{THF})\)

\(\text{CpMn(CO)}_2(\text{THF})\) and \(\text{CH}_2\text{N}_2\)

Figure 3.2: Preparative Reactions  a) \(\text{CpMn(CO)}_2(\text{THF})\)

b) \(\text{CH}_2\text{N}_2\).

with \(\text{CH}_2\text{N}_2\), Figure 3.3. IR spectroscopy showed that photolysis of a \(2 \times 10^{-2}\) M solution of \(\text{CpMn(CO)}_3\) did not result in complete conversion to \(\text{CpMn(CO)}_2(\text{THF})\). In order to have nearly complete conversion one must typically reduce the concentration of \(\text{CpMn(CO)}_3\) to ca. \(5 \times 10^{-3}\) M. In spite of obtaining a nearly complete conversion to \(\text{CpMn(CO)}_2(\text{THF})\), no isolable product was obtained.
Figure 3.3: Preparation scheme of [CpMn(CO)$_2$]$_2$(μ-CH$_2$) using CH$_2$N$_2$. 
Because the preparation of Herrmann et al.\textsuperscript{4} was published in German and quite cumbersome to understand, the expertise of others who had previously prepared the compound was pursued. Several pieces of information proved helpful: the diazomethane must be prepared with 2-(2-ethoxyethoxy)ethanol rather than ethanol\textsuperscript{55c,64} and a Silica column at room temperature with hexane and toluene could be used to isolate $[\text{CpMn(CO)}_2(\mu-\text{CH}_2)]_2$.\textsuperscript{64} Even with the additional information, the compound although present was not present in sufficient quantities to isolate.

Because CH$_2$N$_2$ is an extremely dangerous material that is both severely toxic and explosive,\textsuperscript{7,65} little effort was made to analyze this procedure. Early in the work, when ethanol was used rather than 2-(2-ethoxyethoxy)ethanol, a white precipitate was noted in the receiving flask, which was cooled to ca. -10°C. This was attributed to water which distilled over with the ether.\textsuperscript{55} The use of a higher boiling alcohol, 2-(2-ethoxyethoxy)ethanol, appeared to lessen the distillation of water. The present Aldrich literature\textsuperscript{55a} on the preparation of CH$_2$N$_2$ also neglects to point out that when using 2-(2-ethoxyethoxy)ethanol, the addition of the Diazald solution should be started as soon as ether begins to distill\textsuperscript{55c} rather than waiting until the solvent is heated to 65°C. Waiting results in
a white, polymeric material forming in the reaction flask. A similarly described substance, identified as disodium terephthalate, was found in a preparation which also utilized 2-(2-ethoxyethoxy)ethanol (carbitol).\textsuperscript{65c}

The reaction of CpMn(CO)\textsubscript{2}(THF) with CH\textsubscript{2}N\textsubscript{2} was varied in a variety of ways. Adding excess CpMn(CO)\textsubscript{2}(THF) rather than CH\textsubscript{2}N\textsubscript{2}, blowing Ar over top of the solution to a mineral oil bubbler rather than leaving it open to a bubbler, removing the low-temperature bath versus letting the reaction mixture warm as the bath evaporated, or maintaining the low-temperature bath for an extended period time, did not improve the preparation. Because all of the manipulations of CH\textsubscript{2}N\textsubscript{2} with CpMn(CO)\textsubscript{2}(THF) failed to produce additional [CpMn(CO)\textsubscript{2}]\textsubscript{2}(\mu-CH\textsubscript{2}), the reaction mixture work-up procedure was investigated.

The column involved in the procedure had only yielded sufficient compound to allow for an \textsuperscript{1}H NMR spectrum. As expected,\textsuperscript{64} the elution in hexane of the first two bands, which contain CpMn(CO)\textsubscript{2}(C\textsubscript{2}H\textsubscript{4}) and unreacted CpMn(CO)\textsubscript{3}, took nearly all day. However, during this lengthy process at room temperature the column material may be interacting with the [CpMn(CO)\textsubscript{2}]\textsubscript{2}(\mu-CH\textsubscript{2}), resulting in its decomposition.
Because \([\text{CpMn(CO)}_2\mu-(\text{CH}_2)]\) is air-stable as a solid, it followed that it might not be overly air-sensitive in solution, such that the column could be run at a faster rate without the precautions necessary to exclude air. Thus, using a gas inlet, Ar was used to force the solvent through the column. First, hexane was used to elute the yellow band, until most of it appeared to be through. The solvent was then changed to a mixture of hexane and toluene. The green-brown band began to move at a faster rate. Ultimately, straight toluene was used as the eluent. The green-brown band was evaporated to dryness, resulting in an oil. The separation was not complete; however, pulling a dynamic vacuum on the oil overnight, resulted in the sublimation of \(\text{CpMn(CO)}_3\). Enough material was isolated to perform the recrystallization, which resulted in pure isolated \([\text{CpMn(CO)}_2\mu-(\text{CH}_2)]\). However, the yield, 2%, was still low.

A more recent preparation\(^5\) using an alternative methylenating agent, a sulfur ylide, was reported with a higher yield, 18%. The MeCp analog reaction shows even greater conversion where a yield of 34% was achieved. The preparation involved synthesizing multiple precursors to obtain the desired sulfur ylide, (dimethylamino)phenyloxosulfonium methylide, \((\text{Me}_2\text{N})(\text{Ph})\text{S(O)}=\text{CH}_2\) (Figure 3.4). The last step, Figure 3.4c, did not produce a clean reaction, presumably due to the NaH having an activity of less than one. The ylide is unstable and therefore
Figure 3.4: Preparations of organic precursors of \([\text{CpMn(CO)}_2](\mu-\text{CH}_2)\) preparation

a) S-Methyl S-Phenyl Sulfoximine

b) (Dimethylamino)methylphebyloxosulfonium Fluoroborate

c) (Dimethylamino)phenyloxosulfonium Methylide.
characterization was not possible. In spite of this complication, the reaction of (Me₂N)(Ph)S(O)=CH₂ with CpMn(CO)₂(THF) was conducted (Figure 3.5). The reaction residue was chromatographed in the absence of air on a silica column (2 x 44.5 cm) using first petroleum ether then 9:1 petroleum ether/benzene. Multiple fractions were collected. A red-green band followed a yellow band containing CpMn(CO)₃ and CpMn(CO)₂C₂H₄. The red-green band bled badly making separation difficult. A better separation may have been possible if an appropriate length column (70 cm) had been available. Figure 3.6 shows the evolution of materials from the column where the order of elution is CpMn(CO)₃ (δ 3.89 ppm), CpMn(CO)₂C₂H₄ (δ 3.88 and 1.99 ppm), and finally the product, [CpMn(CO)₂]₂(μ-CH₂) (δ 8.69 and 4.14 ppm). The peak at 0.29 ppm is due to grease. Recrystallization resulted in a 0.14% yield.

This poor yield may be a combination of the reagents used, poor NaH, or the short column, 44.5 rather than 70 cm; thus, the procedure may have potential. The precursors to the ylide are stable and can be prepared in large quantities. Further, the 9:1 petroleum ether/benzene mixture seems to elute the product much more effectively than either the hexane/toluene or toluene solvent systems under the experimental conditions.
Figure 3.5: Preparation scheme of $[\text{CpMn(CO)}_2]_2(\mu-\text{CH}_2)$ using $(\text{Me}_2\text{N})(\text{Ph})\text{S(O)}=\text{CH}_2$. 
Figure 3.6: $^1$H NMR spectra in C$_6$D$_6$ of eluted column fractions (A-F) from (Me$_2$N)(Ph)S(O)=CH$_2$ preparation of [CpMn(CO)$_2$]$_2$(μ-CH$_2$).
Herrmann et al.\textsuperscript{4} also used a 9:1 petroleum ether/benzene mixture. Based on the experiments presented here, it appears that under these column conditions the 9:1 petroleum ether/benzene mixture is preferential for this separation. The hexane and hexane/toluene solvents may work well only on lower temperature columns (ca. 0°C). Because the column appeared to be the critical step in the diazomethane procedure, the yield obtained in the original procedure\textsuperscript{4} is likely to improve with the 9:1 petroleum ether/benzene solvent mixture as well.

A. Evidence of CO-loss Species

1. \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\)

a. Matrix Isolation Studies

Once the compounds were prepared, reactivity studies could be performed. Due to the limited amount of the materials, the initial studies performed were matrix isolation studies, which require very little compound (ca. 2 mg).

Matrix isolation experiments involve freezing a solution of the compound to be studied in a solvent below its glass transition temperature. The solvents chosen (3MP and MCH) freeze without cracking allowing spectral measurements to be obtained. They also do not
absorb strongly in the CO region (1600-2400 cm\(^{-1}\)) of the infrared spectrum, which would obscure the peaks of interest.

Broad band UV-vis irradiation of a 1.0 M solution of \([\text{CpCo}(\text{CO})]_2(\mu-\text{CH}_2)\) in 90% MCH/10% 3MP or neat 3MP at 93-102 K consistently showed that \([\text{CpCo}(\text{CO})]_2(\mu-\text{CH}_2)\) undergoes CO-ligand loss cleanly in frozen hydrocarbon matrices. This was visibly evidenced by a distinct color change from pale red to an intense fuchsia. The infrared spectrum in Figure 3.7 represents the difference before and after 5 minutes of irradiation. The positive peaks at 1810 and 2132 cm\(^{-1}\) show the formation of \([\text{CpCo}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) and free CO,\(^6\) respectively, while the negative peak at 1956 cm\(^{-1}\) is due to the consumption of \([\text{CpCo}(\text{CO})]_2(\mu-\text{CH}_2)\), the starting material (Figure 3.8). The v(CO) at 1810 cm\(^{-1}\) indicates a bridging CO with the structure shown in Figure 3.8. Thus, in frozen solutions we are able to observe \([\text{CpCo}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\).

The Cp* analog of \([\text{CpCo}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\), \([\text{Cp}^*\text{Co}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\), has been structurally characterized. Its single CO stretch occurs at 1758 cm\(^{-1}\).\(^6\) The Cp* ligands donate more electron density to the metal atoms than do the Cp ligands of \([\text{CpCo}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\), which explains the 52 cm\(^{-1}\) shift to lower energy for the Cp* analog. In addition, similar
Figure 3.7: Difference spectrum of \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\). Spectrum after 15 minutes photolysis minus spectrum before photolysis.
alkylidene-bridged complexes, \([\text{CpCo}]_2(\mu-\text{CO})(\mu-\text{CRR'})\) (R, R' = Me, Me; R, R' = Et, Et; R, R' = Me, n-Pr) have been synthesized\(^6\) by several methods, including room temperature photolysis under vacuum or by heating saturated solutions of their respective parent complexes, \([\text{CpCo(CO)}]_2(\mu-\text{CRR'})\).\(^5\) These compounds exhibit increased electron donation to the metal centers, resulting in lower v(CO) values. The frequencies are all between 1795 and 1797 cm\(^{-1}\) (Table 3.1) which is lower in energy than the 1810 cm\(^{-1}\) band observed for \([\text{CpCo]}_2(\mu-\text{CO})(\mu-\text{CH}_2)\) but higher in energy than the 1758 cm\(^{-1}\) stretch of \([\text{Cp}*\text{Co}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\). This reflects the increasing electron donation nature of the ligands where CH\(_2\) < CRR' < Cp*.

Further, the ethylidene-bridged compound, \([\text{CpFe(CO)}]_2(\mu-\text{CO})(\mu-\text{CHCH}_3)\), undergoes CO-loss under nearly identical circumstances to form
Table 3.1: Infrared $v$(CO) Stretches for $[\text{CpCo}]_2(\mu$-$\text{CO})(\mu$-$\text{CH}_2)$ and Isostructural Complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$v$(CO), cm$^{-1}$</th>
<th>Solvent</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{CpCo}]_2(\mu$-$\text{CO})(\mu$-$\text{CH}_2)$</td>
<td>1810</td>
<td>90% MCH/10% 3MP or 3MP</td>
<td></td>
</tr>
<tr>
<td>$[\text{CpCo}]_2(\mu$-$\text{CO})(\mu$-$\text{CMe}_2)$</td>
<td>1797</td>
<td>C$_6$D$_6$</td>
<td>5</td>
</tr>
<tr>
<td>$[\text{CpCo}]_2(\mu$-$\text{CO})(\mu$-$\text{CEt}_2)$</td>
<td>1795</td>
<td>C$_6$D$_6$</td>
<td>5</td>
</tr>
<tr>
<td>$[\text{CpCo}]_2(\mu$-$\text{CO})(\mu$-$\text{C}(\text{Me})(\text{n-Pr})$)</td>
<td>1796</td>
<td>C$_6$D$_6$</td>
<td>5</td>
</tr>
<tr>
<td>$[\text{Cp*Co}]_2(\mu$-$\text{CO})(\mu$-$\text{CH}_2)$</td>
<td>1758</td>
<td>KBr</td>
<td>67</td>
</tr>
</tbody>
</table>

Compounds form bridging ligands upon CO loss. Even $[\text{CpPt(CO)}]_2$ forms $[\text{CpPt}]_2(\mu$-$\text{CO})$ which has a CO bridge between two third row Pt atoms. Dixon et al. have suggested that the formation of bridging dinuclear cyclopentadienyl complexes may be a structural characteristic of the photochemistry of these systems.$^{69}$

The deuterated compound $[\text{CpCo(CO)}]_2(\mu$-$\text{CD}_2)$ was also prepared in order to follow the fate of the methylene protons by observing $v$(CD). The corresponding $v$(CH) stretches are out of the observable window of the hydrocarbon glasses. The $v$(CD) stretches of $[\text{CpCo(CO)}]_2(\mu$-$\text{CD}_2)$ are observed at 2226 and 2138 cm$^{-1}$ (Figure 3.9). As usual, upon irradiation at
Figure 3.9: Infrared spectrum of \([\text{CpCo(CO)}]_2(\mu-\text{CD}_2)\) in 3MP at 99 K.
100 K, [CpCo(CO)]$_2$(µ-CD$_2$) is consumed while [CpCo]$_2$(µ-CO)(µ-CD$_2$) is formed. As shown in Figure 3.10, two new v(CD) bands at 2203 and 2121 cm$^{-1}$ appear that are associated with [CpCo]$_2$(µ-CO)(µ-CD$_2$). The 2203 cm$^{-1}$ band is very weak. The relationship between the consumed v(CO) and formed v(CO) is more clearly seen in Figure 3.11.

If photoejection of the bridging CH$_2$ ligand occurred, ethylene could be formed. Haynes et al. reported the photoejection of ethylene from [(µ-C$_1$, C2)CH$_2$CH$_2$]Os$_2$(CO)$_8$ upon photolysis at 12 K in an Ar matrix to form Os$_2$(CO)$_8$ (Figure 3.12). Because an Ar matrix has no interfering absorbances over the entire spectral range, observation of a weak absorption at 950.1 cm$^{-1}$ resulting from CH$_2$CH$_2$ was possible. Even if a solvent that did not absorb at 950 cm$^{-1}$ were obtained, the observation would be inhibited by the CaF$_2$ windows employed on the hydrocarbon solvent matrix apparatus. Unfortunately, CaF$_2$ absorbs below 1000 cm$^{-1}$.

Because v(CD) bands of CD$_2$CD$_2$ are estimated to be at 2345 (vs) and 2200 (m) cm$^{-1}$, both should be within the hydrocarbon matrix observation window. In principle, the 2345 cm$^{-1}$ resonance could be obscured by residual CO$_2$; however, in the spectra obtained CO$_2$ was not a
Figure 3.10: Difference spectrum of [CpCo(CO)]$_2$(μ-CD)$_2$ in 3MP at 100 K. Spectrum after 5 minutes photolysis minus spectrum before photolysis.
Figure 3.11: Before photolysis of [CpCo(μ-CO)]₂(μ-CD₂), top; Difference after 5 minutes photolysis, below [ν(CD) region].

Figure 3.12: Photoejection of a bridging ligand.

problem. Therefore, no evidence was found for the formation of deuterated ethylene during these photolyses.

Upon allowing the matrix to warm to 281 K, [CpCo]₂(μ-CO)(μ-CH₂) reforms [CpCo(CO)]₂(μ-CH₂). Typically, no other CO containing compounds are observed (Figure 3.8). However, when large concentrations
are employed, such as 3.6 mM, a small amount of CpCo(CO)₂ (2031 and 1971 cm⁻¹) seems to be formed (Figure 3.13). The overwhelming reformation of [CpCo(CO)]₂(μ-CH₂) indicates that the methylene bridge stays intact in the resulting photoproduct. Irradiation of [Cp′Ni(μ-CO)]₂ (Cp′ = C₅H₄Me) at 77 K in a polyvinyl chloride film led to the formation of [Cp′Ni]₂(μ-CO). The suggestion that this product was formed via CO loss was based on its thermal back reaction to starting material upon warming to 150 K. Many other CO-loss species undergo thermal back reaction to their initial parent complexes, including [CpFe]₂(μ-CO)₂(μ-CHCH₃), which also maintains its alkylidene bridge upon CO loss.

Continuing exhaustive irradiation after all [CpCo(CO)]₂(μ-CH₂) is consumed results in an additional CO-loss species. Figure 3.14 shows the formation of free CO (2132 cm⁻¹) and the consumption of [CpCo]₂(μ-CO)(μ-CH₂) (1811 cm⁻¹). Thus, the only CO containing species produced was free CO while [CpCo]₂(μ-CO)(μ-CH₂) was consumed. This suggests the reaction shown in Figure 3.15.

The discovery of the double-CO-loss product, [CpCo]₂(μ-CH₂), comes soon after the report of several new compounds of this type reported in the literature. The complexes, [CpFe(CO)(μ-CO)]₂, Mn₂(CO)₁₀, and
Figure 3.13: Infrared spectrum of the resultant reaction mixture of photolyzed [CpCo(CO)]₂(μ-CD₂) in 3MP at 292 K. The photolysis was performed at 100 K where the reaction mixture was subsequently allowed to warm to 292 K.
Figure 3.14: Difference spectrum of \([\text{CpCo(CO)}]_2(\mu-\text{CD}_2)\) in 3MP at 97 K. Spectrum after 90 minutes photolysis minus spectrum after 60 minutes photolysis.
[CpCo(CO)]_2(\mu-\text{CH}_2) have demonstrated sequential CO loss to form [CpFe(CO)]_2,^{21} \text{Mn}_2(\text{CO})_8,^{73} \text{and } [\text{Cp}^*\text{Fe}(\text{CO})](\mu-\text{CO})(\mu-\text{CH}_2),^{33} \text{respectively. Additionally each double CO-loss product reacts thermally at low temperature to ultimately reform their respective starting materials. Both } [\text{CpFe(CO)}]_2 \text{ and } [\text{Cp}^*\text{Fe(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2) \text{ show thermal back reactions at } 98 \text{ K while } \text{Mn}_2(\text{CO})_8 \text{ back reacts at } 96 \text{ K. Though not explicitly observed spectroscopically, it is reasonable to anticipate that } [\text{CpCo}]_2(\mu-\text{CH}_2) \text{ back reacts with CO to form } [\text{CpCo}]_2(\mu-\text{CO})(\mu-\text{CH}_2). \text{ The schematic of the proposed reactions within under matrix isolation conditions is shown in Figure 3.16.}

On occasion a small peak at 2004 cm\(^{-1}\) would be present in the low temperature solution of [CpCo(CO)]_2(\mu-\text{CH}_2) before photolysis. The band was not seen during the photolysis unless it was present before photolysis. The band also did not grow in in a consistent manner in the matrix
Figure 3.16: Proposed scheme of [CpCo(CO)]_2(μ-CH₂) low temperature matrix photochemistry. The dashed arrow represents a possible thermal reaction not explicitly observed.
experiments in which it was present. Figure 3.17 shows a spectrum of [CpCo(CO)]$_2$(μ-CH$_2$) with the apparent anomalous peak. Because it is not present in the photolyzed solutions unless it is present initially, it is reasonable to assume that this band is due to some impurity in the starting solution which is not consistently present.

There is a stark change in color between [CpCo(CO)]$_2$(μ-CH$_2$) and its CO-loss product, [CpCo]$_2$(μ-CO)(μ-CH$_2$). A low-temperature UV-vis spectrum was acquired of both [CpCo(CO)]$_2$(μ-CH$_2$) and the CO-loss product in 90% MCH/10% 3MP at 100 K. As shown in Figure 3.18, both compounds have three absorption maxima, although the intensities differ. In addition, the bands of the CO-loss product, 320, 369, and 553 nm, are red shifted from those of [CpCo(CO)]$_2$(μ-CH$_2$), 295, 355, and 464 nm. The intense absorption of the CO-loss product at 553 nm probably results in the intense fuchsia color observed.

b. Transient Absorption Spectroscopy at Room Temperature

The production of the CO-loss product, [CpCo]$_2$(μ-CO)(μ-CH$_2$), in a low-temperature matrix gives no indication whether the species will be produced under irradiation at ambient temperatures in solution. However, the IR spectrum definitively defines the structure of the molecule. Because an IR spectrum and UV-vis spectrum can be taken of
Figure 3.17: Irradiation of \([\text{CpCo(CO)}_2(\mu-\text{CH}_2)]\) in 90% MCH/10% 3MP at 98 K. Spectra before (••••••) and after 5 minutes (--------) of photolysis.
Figure 3.18: UV-vis spectra of a 1.0 mM \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) 90% MCH/10% 3MP solution at 98 K (---) and \([\text{CpCo]}_2(\mu-\text{CO})(\mu-\text{CH}_2)\) obtained after 15 minutes photolysis at 100 K (-----).
the same sample in succession, this UV-vis spectrum can then be used as a fingerprint for the existence of this species.\textsuperscript{74}

In transient absorption spectroscopy, a UV-vis spectrum is taken shortly after irradiation. If a photoproduct is still present at the time the UV-vis spectrum is obtained, one can identify the species from the UV-vis spectrum. An optical multichannel analyzer allowed such a measurement to be taken as shortly as 1.4 $\mu$s after a laser pulse. The laser pulse initiated the photochemistry which was monitored by UV-vis spectroscopy. The resultant $\Delta A$ versus wavelength spectrum (Figure 3.19) shows transient absorption maxima at 553 and 400 nm, which is in agreement with the observed low-temperature UV-vis spectrum. Both peaks decayed at about the same rate, suggesting that they are due to the same compound.\textsuperscript{75} A third lower energy band may also have been present but the lamp profile was such that the probing intensity is so low in that region that it could probably not be observed.

c. Related Solution Study with CCl$_4$

Additional evidence for the formation of [CpCo]$_2$(\textmu-CO)(\textmu-CH$_2$) in solution was obtained in the photochemical reaction of [CpCo(CO)]$_2$(\textmu-CH$_2$) in CCl$_4$ solution at 15 to 24°C. As expected, the IR spectra showed a decrease in the peaks associated with [CpCo(CO)]$_2$(\textmu-CH$_2$) and the growth of new peaks. Figure 3.20 shows the IR spectrum of this reaction after 316
Figure 3.19: Transient absorption spectrum of $\text{[CpCo(CO)$_2$(\mu-\text{CH}_2)]}$ in toluene 1.4 $\mu$s after a 308 nm flash.
Figure 3.20: Infrared spectra of the reaction mixture of [CpCo(CO)]$_2$(μ-CH$_2$) and CCl$_4$ in THF after irradiation at ambient temperature immediately after 316 minutes of irradiation (———) and after the solution sat overnight (-----).
minutes of irradiation and after the irradiated solution sat overnight. Both spectra show the peaks due to \( \text{CpCo}(\text{CO})_2 \) at 2021 and 1958 cm\(^{-1}\). The peak at 1976 cm\(^{-1}\) is yet to be assigned while the peak at 1742 cm\(^{-1}\) seems to be related to residual water in the atmosphere. The spectra differ in that the spectrum taken just after 316 minutes of photolysis has peaks at 2126 and 1807 cm\(^{-1}\). These peaks are consistent with the low-temperature hydrocarbon matrix IR band values for free CO, 2133 cm\(^{-1}\), and \( \text{[CpCo]}_2(\mu-\text{CO})(\mu-\text{CH}_2) \), 1810 cm\(^{-1}\), respectively. Their absence in the IR spectrum taken the next morning is an indication of their instability in solution that would be expected for \( \text{[CpCo]}_2(\mu-\text{CO})(\mu-\text{CH}_2) \); it completely back reacts with free CO to form \( \text{[CpCo(CO)]}_2(\mu-\text{CH}_2) \) upon warming to room temperature in the matrix cell. Thus, \( \text{[CpCo]}_2(\mu-\text{CO})(\mu-\text{CH}_2) \) has a sufficient lifetime and can be produced in sufficient quantities at room temperature to be observed by IR spectroscopy.

Other experiments with \( \text{[CpCo(CO)]}_2(\mu-\text{CH}_2) \) and 1% CCl\(_4\) in THF at 0 to 2\(^{\circ}\)C did not yield evidence for the formation of \( \text{[CpCo]}_2(\mu-\text{CO})(\mu-\text{CH}_2) \). This may be due to a fast reaction between THF and \( \text{[CpCo]}_2(\mu-\text{CO})(\mu-\text{CH}_2) \). There is no evidence of a THF substitution complex such as \( \text{Cp(CO)Co(\mu-\text{CH}_2)Co(THF)}\text{Cp} \) at this time, although its formation would be
a plausible explanation for not observing \([\text{CpCo}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) in THF solution while it is clearly present in neat CCl\(_4\).

c. Concluding Remarks

It is clear that \([\text{CpCo}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) is formed both at low temperature and at room temperature. Evidence for a double-CO-loss species has also been obtained within the frozen matrix only. The expectation is that room temperature substitution and alkyne insertion reactions occur because the CO-loss species is the suggested reactive intermediate in these reactions. Many similar systems readily undergo these reactions. In addition, monosubstitution and disubstitution compounds may be able to form at low temperature in the matrix due to the formation of both the single and double-CO-loss species.

2. \([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\)

a. Matrix Photochemistry

\([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\) and \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) are electronically similar, with the exception of the nature of their respective metal based HOMO orbitals. As a result, \([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\) might also expected to undergo CO-loss upon irradiation. Indeed, irradiation of a 1 mM solution of \([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\) in 3MP or in 90% MCH/10% 3MP at 92 to 101 K results in the formation of many new compounds within the first 10
seconds (Figure 3.21). The peaks at 1990 and 1954 cm\(^{-1}\) appear and disappear within 60 seconds (Figure 3.22). Because these bands are so weak (the 1990 cm\(^{-1}\) band never reaches 0.05 Absorbance), they are assumed to be due to a minor product or impurity.

The single-CO-loss species, \([\text{CpMn(CO)}]_2(\mu\text{-CO})(\mu\text{-CH}_2)\), appears within 10 seconds of irradiation with \(\nu(\text{CO})\) stretches at 1900, 1855, and 1788 cm\(^{-1}\). The presence of free CO (2132 cm\(^{-1}\)) is evidence of a CO loss process while the low energy CO resonance (1788 cm\(^{-1}\)) is consistent with a bridging CO ligand. These peaks disappear at about the same rate and are absent from the difference spectrum after 120 seconds of irradiation (Figure 3.22). Thus, if \([\text{CpMn(CO)}]_2(\mu\text{-CO})(\mu\text{-CH}_2)\) is formed at this point, its rate of consumption is equal to its rate of formation. Figure 3.23 shows this initial process.

The structure of \([\text{CpMn(CO)}]_2(\mu\text{-CO})(\mu\text{-CH}_2)\) appears to be analogous to that of \([\text{CpFe(CO)}]_2(\mu\text{-CO})(\mu\text{-CH}_2)\) with the exception of a double Mn-Mn bond rather than a single Fe-Fe bond. The room temperature IR spectrum of \([\text{CpFe(CO)}]_2(\mu\text{-CO})(\mu\text{-CH}_2)\) has three bands at 1986(vs), 1942(vs) and 1780(s) cm\(^{-1}\) in CH\(_2\)Cl\(_2\).\(^{40}\) The \(\nu(\text{CO})\) stretches of \([\text{CpMn(CO)}]_2(\mu\text{-CO})(\mu\text{-CH}_2)\) also correspond well to the ethyldiene-
Figure 3.21: Difference spectrum of \([\text{CpMn(CO)}_2]_2(\mu-\text{CH}_2)\) in 3MP at 97 K. Spectrum after 10 seconds irradiation minus spectrum before irradiation.
Figure 3.22: Difference spectra of [CpMn(CO)$_2$(μ-CH$_2$)] in 3MP at 95-97 K. Spectra after 60 seconds (——) and 120 seconds (--------) irradiation.
The first CO-loss process of \([\text{CpMn(CO)}_2]_2(\mu-\text{CH}_2)\). The bridged complex, \([\text{CpFe(CO)}_2(\mu-\text{CO})(\mu-\text{CH}_3)]\), which has \(v(\text{CO})\) stretches at 1986, 1947, and 1798 cm\(^{-1}\) in 90% MCH/10% 3MP. The \(v(\text{CO})\) stretches of these and other complexes with similar structures are listed in Table 3.2. The \(v(\text{CO})\) stretches at 1962 and 1872 cm\(^{-1}\) also appear to be due to a single species. The bands grow in slowly at first followed by an increase in their rate of formation while the \(v(\text{CO})\) stretches of \([\text{CpMn(CO)}_2(\mu-\text{CO})(\mu-\text{CH}_2)]\) decrease. In addition, the free CO band (2132 cm\(^{-1}\)) continues to increase (Figure 3.22); thus, CO loss is still occurring. These observations suggest that this species may be the product of CO loss from \([\text{CpMn(CO)}_2(\mu-\text{CO})(\mu-\text{CH}_2)]\), as shown in Figure 3.24. The IR \(v(\text{CO})\) bands are consistent with a structure such as \(\text{cis-}[\text{CpMn(CO)}_2(\mu-\text{CH}_2)]\). This all terminal structure with a Mn-Mn triple bond should have a similar structure to \(\text{cis-}[\text{CpCo(CO)}_2(\mu-\text{CH}_2)]\).
Table 3.2: Infrared ν(CO) Stretches for [CpMn(CO)]₂(μ-CO)(μ-CH₂) and Complexes with Similar Structures.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(CO), cm⁻¹</th>
<th>Solvent</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CpMn(CO)]₂(μ-CO)(μ-CH₂)</td>
<td>1900, 1854, 1788</td>
<td>3MP</td>
<td></td>
</tr>
<tr>
<td>[CpFe(CO)]₂(μ-CO)(μ-CH₂)</td>
<td>1986, 1942, 1780</td>
<td>CH₂Cl₂</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>1995, 1957, 1951, 1801</td>
<td>3MP</td>
<td>76</td>
</tr>
<tr>
<td>trans-[Cp*Fe(CO)]₂(μ-CO)(μ-CH₂)</td>
<td>1909, 1758, 1919, 1772</td>
<td>CH₂Cl₂</td>
<td>51</td>
</tr>
<tr>
<td>[CpFe(CO)]₂(μ-CO)(μ-CHCH₃)</td>
<td>1986, 1947, 1798</td>
<td>90% MCH/10% 3MP</td>
<td>77</td>
</tr>
<tr>
<td>cis-[CpFe(CO)]₂(μ-CO)(μ-CCH₂CH₂)</td>
<td>1996, 1961, 1802</td>
<td>hexane</td>
<td>78</td>
</tr>
<tr>
<td>trans-[CpFe(CO)]₂(μ-CO)(μ-CCH₂CH₂)</td>
<td>1954, 1802</td>
<td>hexane</td>
<td>78</td>
</tr>
<tr>
<td>cis-[CpFe(CO)]₂(μ-CO)(μ-C=CH₂)</td>
<td>1998, 1963, 1804</td>
<td>light petroleum</td>
<td>79</td>
</tr>
<tr>
<td>trans-[CpFe(CO)]₂(μ-CO)(μ-C=CH₂)</td>
<td>1957, 1804</td>
<td>light petroleum</td>
<td>79</td>
</tr>
</tbody>
</table>
The cis-only configuration for \([\text{CpMn(CO)}_2(\mu-\text{CH}_2)]\) is proposed based on the relative intensities of the \(\nu(\text{CO})\) IR bands; the high energy band at 1962 cm\(^{-1}\) has greater intensity than the lower energy band at 1872 cm\(^{-1}\). In the cis configuration both the symmetric and asymmetric stretches are allowed. This contrasts with the trans isomer, whose symmetrical stretch is nearly forbidden, typically producing a weak band at high energy, as already discussed with \([\text{CpFe(CO)}(\mu-\text{CO})_2\) and its alkylidene analogs.\(^{33,80}\) Because only two bands are observed, and the high energy band is the most intense, it seems reasonable to suggest the cis isomer. The symmetric trans band could be coincident with the 1962 cm\(^{-1}\) band; however, the rate of change of the two bands (1962 and 1872 cm\(^{-1}\)) appears equivalent, diminishing the likelihood of coincident peaks.

The change in the spectra between irradiation increments first shows the consumption of both \([\text{CpMn(CO)}_2(\mu-\text{CO})(\mu-\text{CH}_2)]\) and the 1990
cm\(^{-1}\) band, as shown in Figure 3.25. However, Figure 3.25 also demonstrates that eventually only the consumption of \([\text{CpMn(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) and a small amount of starting material is observed, with the formation of free CO and v(CO) stretches at 1962 and 1872 cm\(^{-1}\). Therefore, this provides evidence that the double-CO-loss species, cis-\([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\), is at least primarily formed from the single-CO-loss species, \([\text{CpMn(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) (Figure 3.24).

As stated earlier, \([\text{CpFe(CO)}(\mu-\text{CO})]_2\)\(^{21}\) Mn\(_2\text{CO}_{10}\)\(^{73}\) and \([\text{Cp*Fe(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\)\(^{33}\) have all demonstrated double-CO loss in frozen hydrocarbon matrices. The first two formed all terminal structures while the last formed a bridging structure, \([\text{Cp*Fe}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\). In addition, as discussed earlier, \([\text{CpCo}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) also apparently undergoes double-CO loss to form presumably \([\text{CpCo}]_2(\mu-\text{CH}_2)\) in 3MP at 95 K.

The increase in the v(CO) stretches found in cis-\([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\) from those of \([\text{CpMn(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) is not obvious at first. As shown in Figure 3.24, a Mn atom of \([\text{CpMn(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) has four atoms bonded to it excluding the other Mn atom. This would correspond with a tetrahedral arrangement which should allow for reasonable overlap
Figure 3.25: Difference spectra of sequential irradiation increments of \([\text{CpMn(CO)}_2(\mu-\text{CO})(\mu-\text{CH}_2)]\) in 3MP at 95 K. Spectra of irradiation changes between 80 and 60 seconds (---) and 120 and 100 seconds (………).
between the CO $\pi^*$ and M-d orbitals, thus, lowering the energy of the $\nu$(CO) stretches. However, a Mn atom of the double-CO-loss product, cis-[CpMn(CO)]$_2$(μ-CH$_2$), has only 3 bonding atoms excluding the other Mn atom decreasing the overlap between the CO $\pi^*$ and the M-d orbital and thus increasing the $\nu$(CO) stretch.

Eventually, an incremental difference spectrum (Figure 3.26) demonstrates the consumption of the double-CO-loss species [CpMn(CO)]$_2$ (μ-CH$_2$) as well as CpMn(CO)$_3$ (2026 cm$^{-1}$). The consumption of the species associated with $\nu$(CO) stretches at 1941 and 1902 cm$^{-1}$ is not clear. These may be broad bands associated with residual starting material and [CpMn(CO)]$_2$(μ-CO)(μ-CH$_2$). The small ΔA scale makes assessment difficult. However, there is clear formation of additional free CO (2132 cm$^{-1}$) and new species with $\nu$(CO) bands at 1955, 1887, and 1806 cm$^{-1}$.

Because the formation of the CO-loss product CpMn(CO)$_2$ from CpMn(CO)$_3$ is well known in solution and in low temperature matrices,$^{81}$ it seemed likely that the terminal bands observed at 1955 and 1887 cm$^{-1}$ might be due to CpMn(CO)$_2$ formed in the consumption of CpMn(CO)$_3$ (2026 cm$^{-1}$). Thus, to determine the positions of the $\nu$(CO) stretches of CpMn(CO)$_3$ under these conditions, a low temperature photolysis of
Figure 3.26: Difference spectrum of [CpMn(CO)$_2$]$_2$(μ-CH$_2$) in 3MP at 96 K. Spectrum after 5 minutes photolysis minus spectrum after 3 minutes photolysis.
CpMn(CO)₃ was conducted in 90% MCH/10% 3MP at 93 K. The resultant difference spectrum after 15 minutes of photolysis (Figure 3.27) clearly shows the consumption of CpMn(CO)₃ (2026 and 1940 cm⁻¹) with the formation of CpMn(CO)₂ (1954 and 1886 cm⁻¹) and free CO (2132 cm⁻¹). These ν(CO) values correspond very well to the values observed in other low temperature matrix materials such as those shown in Table 3.3. Thus, the ν(CO) bands at 1955 and 1887 cm⁻¹ in Figure 3.26 correspond to the formation of CpMn(CO)₂.

<table>
<thead>
<tr>
<th>Matrix Material</th>
<th>T (K)</th>
<th>ν(CO) (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90% MCH/ 10% 3MP</td>
<td>93</td>
<td>1954, 1886</td>
</tr>
<tr>
<td>Argon⁸¹</td>
<td>12</td>
<td>1972.0, 1903.2</td>
</tr>
<tr>
<td>Methane⁸¹</td>
<td>12</td>
<td>1961.4, 1892.8</td>
</tr>
<tr>
<td>Nitrogen⁸¹ [CpMn(CO)₂N₂]</td>
<td>12</td>
<td>2175.3, 1978.7, 1927.0</td>
</tr>
</tbody>
</table>

Based on the intensities of the CpMn(CO)₃ initially present in the solution and the amount consumed in Figure 3.26, it appears that the CpMn(CO)₂ only arises from CO loss from the CpMn(CO)₃ impurity.
Figure 3.27: Difference spectrum of CpMn(CO)$_3$ in 90% MCH/10% 3MP. Spectrum after 15 minutes photolysis minus spectrum before photolysis.
present in the solution. Now, only a single $v$(CO) band at 1806 cm$^{-1}$ remains to be explained. This band would be consistent with a single CO bridge; thus, it is also possible that cis-[CpMn(CO)]$_2$(μ-CH$_2$) undergoes additional CO loss to form [CpMn]$_2$(μ-CO)(μ-CH$_2$), a triple-CO-loss species (Figure 3.28). The structure of [CpMn]$_2$(μ-CO)(μ-CH$_2$) is consistent with a $v$(CO) resonance of 1806 cm$^{-1}$. This species would contain a formal Mn-Mn quadruple bond. This structure is also consistent with the double CO-loss species, [Cp$^*$Fe]$_2$(μ-CO)(μ-CH$_2$)$_3$ with a bridging rather than semi-bridging-CO group.

![Figure 3.28: The third CO-loss and thermal-back reaction processes of [CpMn(CO)]$_2$(μ-CH$_2$).](image)

Further evidence that [CpMn]$_2$(μ-CO)(μ-CH$_2$) is formed from cis-[CpMn(CO)]$_2$(μ-CH$_2$) is found in Figure 3.29. Here, the matrix was allowed to sit at 96 K for 60 minutes after irradiation was discontinued. The changes that occurred during this 60 minutes are shown in the
Figure 3.29: Difference spectra of [CpMn(CO)$_2$]$_2$(µ-CH$_2$) in 3MP at 96 K. Spectrum after 60 minutes sitting in the dark after irradiation minus spectrum after 10 minutes of irradiation.
difference spectrum. Free CO is consumed along with the resonance at 1806 cm\(^{-1}\), presumably \([\text{CpMn}]_2(\mu\text{-CO})(\mu\text{-CH}_2)\), while \(\text{cis-}[\text{CpMn(CO)}]_2(\mu\text{-CH}_2)\), 1964 and 1872 cm\(^{-1}\), is formed. Because of the formal Mn-Mn quadruple bond is very coordinatively unsaturated, the lack of thermal stability even at 96 K is not surprising.

The conclusions proposed above are not without precedent. Photolysis of \([\text{Cp}^{*}\text{Cr(CO)}]_2\) and \([\text{CpCo(CO)}]_2\) at 12 K in a polyvinyl chloride film resulted in the CO-loss species, \([\text{Cp}^{*}\text{Cr}]_2(\mu\text{-CO})_3\) and \([\text{CpCr}]_2(\mu\text{-CO})_3\), respectively.\(^{72}\) As shown in Figure 3.30, these triply-bridged species contain a formal Cr-Cr quadruple bond. At ca. 80 K these species recombine with CO to form their respective parent complexes or react with THF present in the matrix to form \([\text{Cp}^{*}\text{Cr(\mu-CO)}]_2(\text{CO})(\text{THF})\) and \([\text{CpCr(\mu-CO)}]_2(\text{CO})(\text{THF})\), respectively. Thus, the backreaction noted at 96 K of \([\text{CpMn}]_2(\mu\text{-CO})(\mu\text{-CH}_2)\) is consistent with other photolytically generated quadruple bonded metal dimers.

![Figure 3.30: Structure of [CpCr]_2(\mu-CO)_3](image-url)
The result obtained upon warming the matrix of \([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\) to 305 K is surprising. The IR spectrum obtained (Figure 3.31) contains \(v(\text{CO})\) stretches at 2028, 1965, 1946, 1917, and 1878 cm\(^{-1}\). Thus, \(\text{CpMn(CO)}_3\) (2028 and 1946 cm\(^{-1}\)), \([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\) (1946 and 1917 cm\(^{-1}\)), and \([\text{CpMn(CO)}]_2\) (1965 and 1978 cm\(^{-1}\)) are present upon warming to room temperature. The \(v(\text{CO})\) resonances at 1965 and 1978 cm\(^{-1}\) show the characteristic shift to higher energy upon going to higher temperature. The bands due to \([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\) also fade away within a few hours in solution at room temperature, which corresponds to an expected instability in solution. In addition, when the matrix is immediately cooled again upon reaching room temperature, the \(v(\text{CO})\) bands shift to their respective lower energy assignments.

The stability to 305 K of a triply-bridged metal carbonyl species is not unprecedented. Room temperature photolysis of \([\text{CpCr(CO)}]_2\) in a polyvinyl chloride film produces \([\text{CpCr(CO)}]_2\) \([v(\text{CO})\text{ cm}^{-1}, 1898, 1874]\). This species (Figure 3.32) also contains a Cr-Cr triple bond. Unlike \([\text{CpMo(CO)}]_2\) and \([\text{CpW(CO)}]_2\), \([\text{CpCr(CO)}]_2\) does not back react with CO at room temperature. Thus, a species with four “essentially terminal”
Figure 3.31: Infrared spectrum of the resultant reaction mixture of photolyzed \([\text{CpMn(CO)}_2(\mu-\text{CH}_2)]\) in 90% MCH/10% 3MP at 305 K. The photolysis was performed at 98 K where the reaction mixture was subsequently allowed to warm to 305 K.
CO ligands, which are now considered linear semi-bridging\textsuperscript{31,72,82} and a formal M-M triple bond is stable at room temperature.

\begin{center}
\textbf{Figure 3.32: Structure of [Cp*Cr(CO)\textsubscript{2}]\textsubscript{2}}
\end{center}

The overall reaction scheme proposed is shown in Figure 3.33. The thermal reactivity on warming to room temperature suggests M-M bond cleavage to form CpMn(CO)\textsubscript{3}. Apparently, the methylene may combine with another released methylene to form ethylene, which could be pumped away. The proteo compound provides no convenient IR handle to observe the methylene group in hydrocarbon matrices.

The deuterated complex, [CpMn(CO)\textsubscript{2}(\mu-CD\textsubscript{2})], might allow for observation of the fate of the methylene bridge. As pointed out earlier, the ν(CD) bands of deuterated ethylene would be expected to occur at about 2345 and 2200 cm\textsuperscript{-1}.\textsuperscript{71} In addition, the infrared stretches of Cp*Re\textsuperscript{+}(NO)(PPh\textsubscript{3})(=CH\textsubscript{2})BF\textsubscript{4}\textsuperscript{-} have been reported in KBr.\textsuperscript{83} The ν(=CH\textsubscript{2}) bands are 2987/2972 and 2922 cm\textsuperscript{-1} while the ν(=CD\textsubscript{2}) resonances are 2246/2239 and 2181 cm\textsuperscript{-1}. The high energy C-D stretches of both
Figure 3.33: Proposed scheme of $[\text{CpMn(CO)}_2)_2(\mu-\text{CH}_2)$ low temperature matrix photochemistry. The dashed arrows represent possible thermal routes to the 305 K reaction mixture.
ethylene and Cp*Re+(NO)(PPh$_3$)(=CH$_2$)BF$_4^-$ potentially would still be obscured by residual CO$_2$; however, the low energy bands of each may be observable. Thus, the use of a $\mu$-CD$_2$ bridge may be a method of determining the fate of the methylene group in the matrix.

In the case of [CpMn(CO)$_2$]$_2$(\(\mu\)-CH$_2$), the color change is not as definitive. Whereas [CpCo(CO)]$_2$(\(\mu\)-CH$_2$) showed definitive color change from pale red to fuchsia, [CpMn(CO)$_2$]$_2$(\(\mu\)-CH$_2$) starts pale green and becomes paler upon irradiation. This lack of color is noted in the low-temperature UV-vis spectra obtained of cis-[CpMn(CO)]$_2$(\(\mu\)-CH$_2$), the double-CO-loss species. As seen in Figure 3.34, the UV-vis absorption spectra of both [CpMn(CO)$_2$]$_2$(\(\mu\)-CH$_2$) and cis-[CpMn(CO)]$_2$(\(\mu\)-CH$_2$) have less intense absorptions than either [CpCo(CO)]$_2$(\(\mu\)-CH$_2$) or [CpCo]$_2$(\(\mu\)-CO)(\(\mu\)-CH$_2$) (Figure 3.18). The lack of color noted in [CpMn(CO)]$_2$(\(\mu\)-CH$_2$) is due to its sparse absorption of visible light. Only at 287 and 469 nm does [CpMn(CO)]$_2$(\(\mu\)-CO)(\(\mu\)-CH$_2$) absorb more strongly than [CpMn(CO)$_2$]$_2$(\(\mu\)-CH$_2$). Table 3.4 lists the absorption maxima of [CpMn(CO)$_2$]$_2$(\(\mu\)-CH$_2$) and cis-[CpMn(CO)]$_2$(\(\mu\)-CH$_2$) as well as those of [CpCo(CO)]$_2$(\(\mu\)-CH$_2$) and [CpCo]$_2$(\(\mu\)-CO)(\(\mu\)-CH$_2$).
Figure 3.34: UV-vis spectra of a 1.0 mM \([\text{CpMn(CO)}_2(\mu-\text{CH}_2)\text{3MP}]\) solution at 98 K (-----) and \([\text{CpMn(CO)}_2(\mu-\text{CH}_2)]\) obtained after 10 minutes photolysis at 94 K (-------).
Table 3.4: UV-vis Absorption Maxima for Parent Methylene-Bridged Species and Selected CO-loss Products

<table>
<thead>
<tr>
<th>Compound</th>
<th>Maxima (nm)</th>
<th>Solvent; T (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CpCo(CO)]₂(μ-CH₂)</td>
<td>295, 355, 464</td>
<td>90% MCH/10% 3MP; 93</td>
</tr>
<tr>
<td>[CpCo]₂(μ-CO)(μ-CH₂)</td>
<td>320, 369, 553</td>
<td>90% MCH/10% 3MP; 93</td>
</tr>
<tr>
<td>[CpMn(CO)]₂(μ-CH₂)</td>
<td>404, 572</td>
<td>3MP; 98</td>
</tr>
<tr>
<td>[CpMn(CO)]₂(μ-CH₂)</td>
<td>287, 369, 469</td>
<td>3MP; 98</td>
</tr>
<tr>
<td>[Cp*Fe(CO)]₂(μ-CO)(μ-CH₂)³³</td>
<td>322, 542</td>
<td>3MP; 93</td>
</tr>
<tr>
<td>[Cp*Fe]₂(μ-CO)₂(μ-CH₂)³³</td>
<td>482</td>
<td>3MP; 93</td>
</tr>
</tbody>
</table>

b. Transient Absorption Spectroscopy at Room Temperature

As was the case in the Co complex, an optical multichannel analyzer was used to obtain a transient absorption spectrum of photolyzed [CpMn(CO)]₂(μ-CH₂). These experiments will indicate whether the double-CO-loss species, [CpMn(CO)]₂(μ-CH₂), is present under ambient solution photolysis conditions. Figure 3.35 shows the transient absorption spectrum of [CpMn(CO)]₂(μ-CH₂), taken 2 μs after a 308 nm laser flash. The most prominent feature of this spectrum is the negative peak at 404 nm, which is due to the consumption of [CpMn(CO)]₂(μ-CH₂). A slightly positive peak at 469 nm suggests the formation of a new complex. Some correspondence exists of the transient spectrum to the differences in the
Figure 3.35: Transient absorption spectrum of [CpMn(CO)$_2$]($\mu$-CH$_2$) in 90% MCH/10% 3MP 2 $\mu$s after a 308 nm flash.
absorptions of [CpMn(CO)₂]₂(μ-CH₂) and [CpMn(CO)]₂(μ-CH₂) shown in Figure 3.34. This observation seems consistent with the presence of the double-CO-loss complex.

[CpMn(CO)₂]₂(μ-CH₂) decomposes under these conditions; however, comparison of single flash spectra suggest this transient spectrum is reasonable. The intensity is low, which is not surprising because cis-[CpMn(CO)]₂(μ-CH₂) does not absorb much more strongly than [CpMn(CO)]₂(μ-CH₂) at any λ between 250 and 750 nm. Although the difference at 287 nm is outside the profile of the lamp, the increased absorbance at 404 of [CpMn(CO)₂]₂(μ-CH₂) appears as a negative ΔA peak while the increased absorption of [CpMn(CO)]₂(μ-CH₂) at 469 nm may appear as a slightly positive ΔA peak at ca. 490 nm in the transient spectrum. The occurrence of a positive peak at ca. 655 nm of the approximate magnitude of the 490 nm peak does not correspond to the observed UV-vis spectral differences. If the apparent peak at ca. 655 nm is not a peak at all, but rather defines the baseline, there would not be a peak at 490 nm. Thus, the transient absorption spectrum is less clear in its support of the existence of [CpMn(CO)]₂(μ-CH₂) under ambient solution photolysis conditions than in the case of [CpCo]₂(μ-CO)(μ-CH₂).
c. Concluding Remarks

The transient spectrum of \([\text{CpMn(CO)}_2]_2(\mu-\text{CH}_2)\) cannot be used as strong support of the formation of a CO-loss species at room temperature. However, the evidence for the formation of not only a single-CO-loss species, but a double and perhaps triple-CO-loss species is compelling at low temperature in a hydrocarbon matrix. Solution reactivity studies still have the potential to support indirectly the existence of a CO-loss product in solution.\(^{22}\) The double CO-loss species, \(\text{cis-[CpMn(CO)}_2]_2(\mu-\text{CH}_2)\), appears to be stable to room temperature; this may eventually allow more detailed characterization of its structure. These studies may reveal a similar structure to that of \([\text{CpCr(CO)}_2]_2\) (Figure 3.32) where the CO ligands have a Cr-Cr-C angle of 73.0 and 79.1° that probably protect the M-M bond.

3. \([\text{Cp*Fe(CO)}_2(\mu-\text{CO})(\mu-\text{CH}_2)\]

Another interesting methylene-bridged complex is \([\text{Cp*Fe(CO)}_2(\mu-\text{CO})(\mu-\text{CH}_2)\]). Due to the steric crowding the complex resulting from the Cp* (C\(_5\)Me\(_5\)) ligands, the complex adopts a trans-only configuration.\(^{51}\) This greatly simplifies its IR spectrum, making the complex ideal for matrix isolation studies.
The complex \([\text{Cp}^\#\text{Fe(\text{CO})}_2(\mu-\text{CO})(\mu-\text{CH}_2)]\) has previously been shown to undergo sequential CO loss in a 3MP matrix at 93 K (Figure 3.36).\(^{33}\) The double-CO-loss product, \([\text{Cp}^\#\text{Fe}_2(\mu-\text{CO})(\mu-\text{CH}_2)]\), was observed to thermally back react to the single-CO-loss species, \([\text{Cp}^\#\text{Fe}_2(\mu-\text{CO})_2(\mu-\text{CH}_2)]\) at temperatures as low as 98 K; thus, the species is highly reactive with two electron donors such as CO. Many other CO-loss species have been shown to interact with 2 electron donating ligands in a low temperature matrix.\(^{81,84}\) Thus, \([\text{Cp}^\#\text{Fe}_2(\mu-\text{CO})(\mu-\text{CH}_2)]\) would be expected to react with other 2 electron donors such as phosphines. In this study, \(\text{P(n-Bu)}_3\) was employed to explore this possibility because it is readily available and soluble in 3MP at 95 K.

a) Matrix Reactivity with \(\text{P(n-Bu)}_3\)

The reaction of the double-CO-loss species, \([\text{Cp}^\#\text{Fe}_2(\mu-\text{CO})(\mu-\text{CH}_2)]\), with \(\text{P(n-Bu)}_3\) was followed at 95 K in a frozen 3MP matrix. This reaction is facile at this temperature. The net reaction after 4 hours of irradiation is demonstrated in Figure 3.37 where free CO and a species with a bridging CO peak appear at 2133 and 1701 cm\(^{-1}\), respectively, while the negative peaks at 1916 and 1765 cm\(^{-1}\) indicate that \([\text{Cp}^\#\text{Fe(\text{CO})}_2(\mu-\text{CO})(\mu-\text{CH}_2)]\) is consumed.
Figure 3.36: Scheme of photochemical and thermal reaction pathways of \([\text{Cp}^*\text{Fe(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\).\textsuperscript{33}
Figure 3.37: Infrared difference spectrum of $[\text{Cp}^*\text{Fe(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)$ and $\text{P(n-Bu)}_3$ after 4 hours of irradiation.
This reaction does not appear to occur in one step, however. Figure 3.38 compares successive difference spectra of the reaction between 60 and 40 minutes and 40 and 20 minutes. These spectra illustrate the formation and consumption of CO-loss complexes during this reaction. In the \(t = 40 - t = 20\) spectrum, \([\text{Cp}^*\text{Fe(CO)}]_2(\mu\text{-CO})(\mu\text{-CH}_2)\) and \([\text{Cp}^*\text{Fe}]_2(\mu\text{-CO})_2(\mu\text{-CH}_2)\) are consumed while the double CO-loss species, \([\text{Cp}^*\text{Fe}]_2(\mu\text{-CO})(\mu\text{-CH}_2)\) (1727 cm\(^{-1}\)), and a new species (1701 cm\(^{-1}\)) show a net increase. This contrasts the \(t = 60 - t = 40\) spectrum for which \([\text{Cp}^*\text{Fe(CO)}]_2(\mu\text{-CO})(\mu\text{-CH}_2)\), \([\text{Cp}^*\text{Fe}]_2(\mu\text{-CO})_2(\mu\text{-CH}_2)\), and \([\text{Cp}^*\text{Fe}]_2(\mu\text{-CO})(\mu\text{-CH}_2)\) show net consumption while the new species continues to be formed faster than it is consumed. Previous matrix photochemistry performed under these conditions in the absence of \(\text{P(n-Bu)}_3\) does not show this peak at 1701 cm\(^{-1}\). It is therefore concluded that this species is the result of a dinuclear species that contains a bridging CO group and a \(\text{P(n-Bu)}_3\) ligand.

In addition, the new species is not observed before the formation of \([\text{Cp}^*\text{Fe}]_2(\mu\text{-CO})(\mu\text{-CH}_2)\) (Figure 3.39). Thermally, at 95 K the consumption of \([\text{Cp}^*\text{Fe}]_2(\mu\text{-CO})(\mu\text{-CH}_2)\) is noted with the formation of the new species (Figure 3.40). Further, when considering the 18 electron rule, a
Figure 3.38: Difference spectra of sequential irradiation increments of \([\text{Cp}^*\text{Fe}(\text{CO})_2\mu-\text{CO})(\mu-\text{CH}_2)\) and \(\text{P(n-Bu)}_3\) in 3MP at 95 K. Spectra of irradiation changes between 20 and 40 minutes (-----) and 40 and 60 minutes (———).
Figure 3.39: Irradiation of \([\text{Cp}^*\text{Fe(CO)}_3]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) and \(\text{P(n-Bu)}_3\) in 3MP at 94 K. Spectra after 6 minutes (------) and 20 minutes (-----) irradiation.
Figure 3.40: Difference spectrum of the thermal reaction between 30 and 60 minutes after irradiation of \([\text{Cp}^*\text{Fe(CO)}_2(\mu-\text{CO})(\mu-\text{CH}_2)] + \text{P(n-Bu)}_3\). Spectrum after 60 minutes minus spectrum after 30 minutes.
reasonable structure for a monosubstituted dinuclear species is difficult to imagine without a terminal CO group. Thus, it is concluded that this new species is \([\text{Cp}^*\text{Fe}\{\text{P(n-Bu)}_3]\}_2(\mu-\text{CO})(\mu-\text{CH}_2)\) (Figure 3.41). This complex is the first disubstituted species of this type. Photochemically, other cyclopentadienyl dinuclear complexes such as \([\text{CpFe(CO)}(\mu-\text{CO})]_2\) only form monosubstituted phosphine complexes.\(^{24}\) No explanation has been found in the literature to explain this phenomenon. It is possible that the nature of the organometallic framework in the unique environment of the matrix, low temperature and high viscosity with prolonged irradiation, allow this product to be formed.

![Figure 3.41: Structures of \([\text{Cp}^*\text{Fe}\{\text{P(n-Bu)}_3]\}_2(\mu-\text{CO})(\mu-\text{CH}_2)\) and \((\text{CO})\text{Cp}^*\text{Fe}(\mu-\text{CO})(\mu-\text{CH}_2)\text{FeCp}^*\{\text{P(n-Bu)}_3\}].

The nature of the bridging carbonyl in \([\text{Cp}^*\text{Fe}\{\text{P(n-Bu)}_3]\}_2(\mu-\text{CO})(\mu-\text{CH}_2)\) is either bridging or semi-bridging. Sometimes the assignment can be estimated based on the carbonyl band location alone.\(^{85}\) However, because the \(\text{Cp}^*\) and \(\text{P(n-Bu)}_3\) donate substantial electron density, a band
at 1701 cm$^{-1}$ may still be due to a normal bridge that is perpendicular to the M-M bond. Under many circumstances, a crystal structure allow us to distinguish between bridging and semi-bridging carbonyls.$^{86}$ However, this method is not available for species that are only present in a matrix or solution. Fortunately, plane-polarized-light photolyses can often be employed to determine whether the CO is perpendicular to the M-M axis or not. Among other complexes,$^{87}$ this method has been successfully employed on [CpPt]$_2$(μ-CO) in a N$_2$ matrix.$^{69}$ This may be a method to derive the nature of the bridging carbonyl on this and other matrix-dwelling molecules for which there is a question concerning the semi-bridging assignment,$^{33}$ such as [Cp*Fe]$_2$(μ-CO)(μ-CH$_2$)$_2$.$^{88}$

Some suggestion of the monosubstituted complex, (CO)Cp*Fe(μ-CO)(μ-CH$_2$)FeCp*[P(n-Bu)$_3$] (Figure 3.41), is evident upon close examination of the matrix spectra. The bridging CO band of this complex may be the one at 1779 cm$^{-1}$ while its terminal CO band could be coincident with the 1929 cm$^{-1}$ band of [Cp*Fe(CO)]$_2$(μ-CO)(μ-CH$_2$). After all of [Cp*Fe(CO)]$_2$(μ-CO)(μ-CH$_2$) is consumed (absence of 1916 and 1765 cm$^{-1}$ peaks), the band at 1929 cm$^{-1}$ remains along with a peak at 1779 cm$^{-1}$. The latter band is obscured in the difference spectra by a peak of
band is visible (Figure 3.37). The initial growth rate of (CO)Cp*Fe(\(\mu\)-CO)(\(\mu\)-CH\(\_\)2)FeCp*[P(n-Bu)\(_3\)] cannot be determined because the terminal peak is obscured, and the bridging peak begins as a shoulder on the 1765 cm\(^{-1}\) peak of both [Cp*Fe(CO)]\(_2\)(\(\mu\)-CO)(\(\mu\)-CH\(\_\)2) and [Cp*Fe]\(_2\)(\(\mu\)-CO)\(_2\)(\(\mu\)-CH\(\_\)2).

Once all of the [Cp*Fe(CO)]\(_2\)(\(\mu\)-CO)(\(\mu\)-CH\(\_\)2) is consumed after 140 minutes irradiation (Figure 3.42), the terminal band (1929 cm\(^{-1}\)) remains reasonably constant (\(\Delta A = .006\)) throughout the following 100 minutes of irradiation and 90 minutes of sitting in the dark. The bridging CO band (1779 cm\(^{-1}\)) remains after 240 minutes of irradiation, after which nearly all of [Cp*Fe]\(_2\)(\(\mu\)-CO)\(_2\)(\(\mu\)-CH\(\_\)2) is consumed (Figure 3.43). It is possible that these peaks correspond to the formation of (CO)Cp*Fe(\(\mu\)-CO)(\(\mu\)-CH\(\_\)2)FeCp*[P(n-Bu)\(_3\)]. However, a band shift to higher energy (1929 and 1779 cm\(^{-1}\) from 1916 and 1772 cm\(^{-1}\)) is observed rather than a shift lower energy, which would be expected upon phosphine substitution. The shift to higher energy may be the result of matrix cage effects.

The complexes, (CO)Cp*Fe(\(\mu\)-CO)(\(\mu\)-CH\(\_\)2)FeCp*[P(n-Bu)\(_3\)] and [Cp*Fe[P(n-Bu)\(_3\)]\(_2\)(\(\mu\)-CO)(\(\mu\)-CH\(\_\)2) appear to be present upon warming to room temperature (Figure 3.44), which suggests that they are at least
Figure 3.42: Infrared spectrum of [Cp*Fe(CO)]$_2$(μ-CO)(μ-CH$_2$) and P(n-Bu)$_3$ after 140 minutes of irradiation in 3MP at 95 K.
Figure 3.43: Infrared spectrum of $[\text{Cp}^*\text{Fe(CO)}_2(\mu-\text{CO})(\mu-\text{CH}_2)]$ and $\text{P(n-Bu)}_3$ after 240 minutes of irradiation in 3MP at 95 K.
Figure 3.44: Infrared spectrum of the resultant reaction mixture of photolyzed \([\text{Cp}^*\text{Fe(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) and \(\text{P(n-Bu)}_3\) in 3MP at 292 K. The photolysis was performed at 95 K after which the reaction mixture was allowed to warm.
reasonably kinetically stable. The warmed spectrum shows the formation of starting material (1919 and 1772 cm\(^{-1}\)), a weak band at 1971 cm\(^{-1}\), a medium band at 1931 cm\(^{-1}\), and a strong peak at 1711 cm\(^{-1}\). The peak at 1971 cm\(^{-1}\) corresponds well to cis-[Cp*Fe(CO)]\(_2\)(µ-CO)(µ-CH\(_2\)) which was shown to form previously under similar conditions (1972 cm\(^{-1}\)).\(^{76}\) The 1931 cm\(^{-1}\) band is likely due to the monosubstitution product where a slight shift to higher energy, relative to 1929 cm\(^{-1}\), is typical upon warming while the bridging CO band is probably buried under the broad peak at 1772 cm\(^{-1}\). The \(v\)(CO) bands compare reasonably with those reported for the monosubstituted ethylidene complex, Cp\(_2\)Fe\(_2\)(CO)(µ-CO)\(_2\)[P(n-Bu)\(_3\)], which has two CO stretches. These bands appear at 1920 and 1745 cm\(^{-1}\) in toluene,\(^{77}\) at 1934 and 1747 cm\(^{-1}\) in hexane,\(^{24}\) at 1920 and 1730 cm\(^{-1}\) in THF,\(^{34}\) and at 1933 and 1746 cm\(^{-1}\) in cyclohexane.\(^{89}\)

The 10 cm\(^{-1}\) shift of [Cp*Fe{P(n-Bu)\(_3\)}\(_2\)(µ-CO)(µ-CH\(_2\)) from 1701 to 1711 cm\(^{-1}\) due to matrix warming is somewhat large as compared to other systems.\(^{90}\) However, the shift to higher energy upon increased temperature is consistent with the systems presented earlier, suggesting that the bisphosphine complex, [Cp*Fe{P(n-Bu)\(_3\)}\(_2\)(µ-CO)(µ-CH\(_2\)), is also present at 292 K. In addition, a shift to lower energy is expected for a
mono-to a di-substituted phosphate. A 54 cm\(^{-1}\) shift to lower energy is reported for the bridging CO band in the monosubstituted complex, \(\text{Cp}_2\text{Fe}_2(\text{CO})(\mu-\text{CO})(\mu-\text{CHCH}_3)[\text{P(n-Bu)}_3]\), relative to the parent complex, \(\text{Cp}_2\text{Fe}_2(\text{CO})(\mu-\text{CO})(\mu-\text{CHCH}_3)\) in THF\(^{34}\). The shift from parent-to di-substitution for the \(\text{trans}-[\text{Cp}^*\text{Fe(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) system is 61 cm\(^{-1}\); it is very likely that the second phosphine has a greater effect on the observed v(CO) resonance because there is now only one CO available for backbonding.

A proposed scheme of the formation of \([\text{Cp}^*\text{Fe(P(n-Bu)}_3)]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) is shown in Figure 3.45. With the present data, it is not clear whether \([\text{Cp}^*\text{Fe}_2(\mu-\text{CO})(\mu-\text{CH}_2)\) goes directly to the disubstituted species or goes through the monosubstituted intermediate. A slight shoulder on the 1765 cm\(^{-1}\) peak is apparent after 6 minutes of irradiation before the bisphosphine complex appears (1701 cm\(^{-1}\)). However, the bisphosphine grows in at a much faster rate once it appears, indicating that it may form directly from \([\text{Cp}^*\text{Fe}_2(\mu-\text{CO})(\mu-\text{CH}_2)\) as well as from the monophosphine complex.

A similar question arose in the photosubstitution\(^{91}\) reactions of \([\text{CpMo(CO)}_3]_2\) with PPh\(_3\) to form \([\text{CpMo(CO)}_2\text{PPh}_3]_2\). Initially, a radical
Figure 3.45: Proposed Scheme for the photochemical and thermal reaction pathways of \([\text{Cp}^*\text{Fe}^{}(\text{CO})_2(\mu-\text{CO})(\mu-\text{CH}_2)(\text{L})]\) and \(\text{P}(n\text{-Bu})_3\) in low temperature matrices.
mechanism involving homonuclear cleavage of the M-M bond was suggested.92 Once the photochemically induced CO-loss species, 
[CpMo(CO)]_2(\mu-\text{CO})_2(\mu-\eta^1,\eta^2-\text{CO}), was detected,17 a possible double-CO-loss mechanism was suggested.93 Recently, however, a laser flash photolysis study by Knorr and Brown94 have shown that [CpMo(CO)]_2(\mu-\text{CO})_2(\mu-\eta^1,\eta^2-\text{CO}) undergoes thermal CO loss to form [CpMo(CO)]_2, and CO addition to form [CpMo(CO)]_3 with no indication of a photochemical double-CO-loss product. In addition, a time-resolved IR spectroscopy study of the photochemistry of [CpMo(CO)]_3 was performed by Peters, George, and Turner.75 They supported the conclusions of Knorr and Brown and showed no evidence of a double-CO-loss species at 1 \mu s after the flash.

Thus, to date it appears that the photosubstitution of [CpMo(CO)]_3 may be due to the addition of L to [CpMo(CO)]_2(\mu-\text{CO})_2(\mu-\eta^1,\eta^2-\text{CO}) followed by thermal CO dissociation and the addition of a second L. However, no studies have been reported following the sequential addition of L. In principle, time-resolved IR spectroscopy should be able to detect a monosubstituted complex and determine whether the next CO is lost thermally or photochemically.
b. Transient Absorption Spectroscopy of \([\text{Cp}^*\text{Fe(CO)}_2]_2(\mu-\text{CO})(\mu-\text{CH}_2)\)

Simply because a time-resolved method does not detect a species does not exclude its formation under different circumstances. For instance, the transient absorption spectra of \([\text{Cp}^*\text{Fe(CO)}_2]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) obtained 2 \(\mu\)s after a 308 nm laser flash shows the formation of the single-CO-loss complex, \([\text{Cp}^*\text{Fe}]_2(\mu-\text{CO})_2(\mu-\text{CH}_2)\) with no indication of another species (Figure 3.46). The \(\Delta\) absorption maximum at 490 and 650 nm correspond clearly to the greater \(\epsilon\) of \([\text{Cp}^*\text{Fe}]_2(\mu-\text{CO})_2(\mu-\text{CH}_2)\) than \([\text{Cp}^*\text{Fe(CO)}_2]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) at these wavelengths (Figure 3.47). However, under prolonged irradiation at 93 K the double-CO-loss species, \([\text{Cp}^*\text{Fe}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\), is formed usually within 10 minutes of irradiation.\(^{76}\) Obviously, the matrix isolation experiment with prolonged irradiation, low temperature, and viscous medium allow different processes to occur as compared to a short laser flash at room temperature.

c. Concluding Remarks

As of now, there have been no reports of the solution reactions of \([\text{Cp}^*\text{Fe(CO)}_2]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) with phosphines and other two electron donors. Due to the existence of the single-CO-loss species within 1.4 \(\mu\)s of the laser flash, formation of a double CO-loss species in the low temperature matrix, and its facile reaction with phosphines at 96 K, it
Figure 3.46: Transient absorption spectrum of \([\text{Cp}^*\text{Fe(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) in cyclohexane 2.0 μs after a 308 nm flash.
Figure 3.47: UV-vis spectra of $[\text{Cp}^*\text{Fe(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)$ (——) and $[\text{Cp}^*\text{Fe}]_2(\mu-\text{CO})_2(\mu-\text{CH}_2)$ (· · · · · · ·) in 3MP at 93 K. 33
seems obvious that the photochemical solution studies of [CpFe(CO)]_2(μ-CO)(μ-CHCH_3)\textsuperscript{22,34} with phosphines, phosphites, and alkynes should be able to be extended to [Cp*Fe(CO)]_2(μ-CO)(μ-CH_2). Because of the similarities of two the complexes, nearly identical patterns of phosphine substitution and alkyne insertion might be expected.

B. Solution Reactivity with Alkynes and Phosphorus-Containing Molecules

The CO-loss products of dinuclear inorganic compounds are the intermediates in the formation of their substitution compounds involving phosphorus-containing compounds and their insertion products with alkynes. Bursten et al.\textsuperscript{23} have demonstrated the role of single-loss products through laser flash photolysis kinetic studies of [CpFe(CO)(μ-CO)]_2 and [CpFe(CO)]_2(μ-CO)(μ-CHCH_3) with phosphines and alkynes. Their proposed mechanistic scheme is shown in Figure 1.13. Zhang and Brown\textsuperscript{24} have observed a species in a laser flash photolysis experiment that they believe may be an η^2-bound alkyne intermediate in the proposed insertion mechanism. Thus, because [CpCo(CO)]_2(μ-CH_2), [CpMn(CO)]_2(μ-CH_2), and [Cp*Fe(CO)]_2(μ-CO)(μ-CH_2) all form CO-loss species, they should undergo substitution and insertion reactions as well.
Surprisingly, many alkynes do not show the clean photochemical reactivity with \([\text{CpCo}(\text{CO})_2(\mu-\text{CH}_2)]\) that is expected. However, this observation does not mean that under different reactions conditions they will not undergo a reaction. For example, Pettit et al. reported that the ethylidene complex \([\text{CpFe}(\text{CO})_2(\mu-\text{CO})(\mu-\text{CHCH}_3)]\) did not react thermally or photochemically with \(\text{PPh}_3\).\(^{34}\) This result contrasts with more recent work in which \([\text{CpFe}(\text{CO})_2(\mu-\text{CO})(\mu-\text{CHCH}_3)]\) was found to react photochemically with \(\text{PPh}_3\) to form the mono-substituted product, \([\text{Cp(CO)}\text{Fe}(\mu-\text{CO})(\mu-\text{CHCH}_3))\text{Fe(PPh}_3\text{Cp}])\).\(^{22}\)

### 1. Reactions of Alkynes with \([\text{CpCo}(\text{CO})_2(\mu-\text{CH}_2)]\)

**a. Maleic Anhydride**

An NMR tube reaction of \([\text{CpCo}(\text{CO})_2(\mu-\text{CH}_2)]\) with maleic anhydride did not show evidence of a reaction after one hour. Additional irradiation yielded a decrease in \([\text{CpCo}(\text{CO})_2(\mu-\text{CH}_2)]\) with a fine precipitate. Other than a small IR band at 2021 cm\(^{-1}\) in toluene, there was no indication of significant reactivity.

**b. 1-hexyne**

Irradiation of \([\text{CpCo}(\text{CO})_2(\mu-\text{CH}_2)]\) in the presence of 1-hexyne in THF solution resulted in the probable formation of \(\text{CpCo}(\text{CO})_2\) as indicated
by IR (2021 and 1953 cm\(^{-1}\)). The UV-cabinet did feel warm as the irradiation progressed. Therefore, thermal contributions cannot be ruled out in this reaction. Ultimately, the solution became murky suggesting decomposition to Co metal. No evidence of the production of a metal-alkyne complex was found under these conditions.

c. Phenylacetylene (PHAC)

Via IR spectroscopy, little change was noted after 6 hours of irradiating a solution of [CpCo(CO)]\(_2\)(\(\mu\)-CH\(_2\)) and phenylacetylene. However, upon examination of the reaction tube, a purple film was found. Upon cannulating the red supernatant solution from the reaction tube, a green powder was observed.

The IR and NMR resonances of the green solid residue and the toluene solution residue are noted in Table 2.1. These bands provide some evidence for the formation of [CpCo(CO)]\(_2\)(\(\mu\)-CO), which is a photoproduct of CpCo(CO)\(_2\).\(^{42,44}\) The peaks at 2021(w) and 1953(s) cm\(^{-1}\) in THF could be due to CpCo(CO)\(_2\) (Table 3.5), but the 1953 cm\(^{-1}\) is likely coincident with another species due to its weak intensity compared to the 2021 cm\(^{-1}\) peak. In CpCo(CO)\(_2\), the two peaks are of about equal intensity. Thus, three additional peaks at 1953(s), 1995(w) and 1819(m) cm\(^{-1}\) are due to other species. The 1953 and 1819 cm\(^{-1}\) peaks might be attributed to
[CpCo(CO)]$_2$(µ-CO). The assigned IR Nujol mull bands of [CpCo(CO)]$_2$(µ-CO) are 1965 and 1814 cm$^{-1}$. Finally, the 1995 cm$^{-1}$ peak may be due to CpCo(CO)(η$^2$-CH$_2$CH$_2$). Lee and Brintzinger reported the photochemical reaction of diphenylacetylene with CpCo(CO)$_2$ and found CpCo(CO)(η$^2$-C$_2$Ph$_2$), which has a single CO resonance at 1990 cm$^{-1}$ in toluene, as one of the photoproducts.

It appears that some incorporation of the phenylacetylene molecule in [CpCo(CO)]$_2$(µ-CH$_2$) may have occurred because of the phenyl resonances at 7.8 and 7.5 ppm in the C$_6$D$_6$ $^1$H NMR. These resonances hydrogens is not clear. If the phenylacetylene inserted between the methylene C and a Co atom, the resonance could be the one at 7.89 ppm.

Table 3.5: Various Reported $\nu$(CO) Bands of CpCo(CO)$_2$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\nu$(CO) (cm$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>THF</td>
<td>2021, 1958</td>
</tr>
<tr>
<td></td>
<td>2020, 1960$^{4a}$</td>
</tr>
<tr>
<td></td>
<td>2020, 1955$^{96}$</td>
</tr>
<tr>
<td>Toluene</td>
<td>2023, 1960</td>
</tr>
<tr>
<td></td>
<td>2025, 1970$^{95}$</td>
</tr>
<tr>
<td>3MP</td>
<td>2031, 1971$^{97}$</td>
</tr>
</tbody>
</table>
The phenylacetylene hydrogen would be expected to be downfield around 12 ppm based on the acetylene insertion product, \( \text{Cp}_2\text{Fe}_2(\text{CO})(\mu\text{-CO})(\mu\eta^1,\eta^3\text{-C}_2\text{H}_2\text{CHCH}_3) \) (Figure 3.48), in which the proton attached to the \( \eta^1 \) C has a \(^1\text{H}\) resonance at 11.86 ppm in \( \text{CDCl}_3 \).\(^{26}\) Additionally, the PHAC proton in the PHAC insertion product of \( [\text{CpFe(CO)(\mu-CO)}]_2 \), \( \text{Cp}_2\text{Fe}_2(\text{CO})(\mu\text{-CO})(\mu\sigma\eta^2\text{-C(O)CR'CR}) \) (\( \text{R'}=\text{Ph}, \text{R}=\text{H} \)) (Figure 3.48), occurs at 12.83 ppm in \( \text{CDCl}_3 \).\(^{25}\) Acetylene and phenylacetylene both form dimetallabutenone type insertion products upon reaction with \([\text{CpFe(CO)(\mu-CO)}]_2\); insertion product structures are discussed in the introduction. The spectral area analyzed in this study extends to 10 ppm; thus, no assessment at this time can be made with regards to the presence of peaks further downfield.

![Figure 3.48: \( \text{Cp}_2\text{Fe}_2(\text{CO})(\mu\text{-CO})(\mu\eta^1,\eta^3\text{-C}_2\text{H}_2\text{CHCH}_3) \) and \( \text{Cp}_2\text{Fe}_2(\text{CO})(\mu\text{-CO})(\mu\sigma\eta^2\text{-C(O)CR'CR}) \).](image)
There are a pair of peaks likely due to the Cp rings at 4.76 and 4.48 ppm in C₆D₆; the Cp ¹H peaks of Cp₂Fe₂(CO)(μ-CO)(μ-η¹,η³-C₂H₂CHCH₃) occur at 4.71 and 4.36 ppm in CDCl₃. The presence of phenyl group resonances are also consistent with an insertion product. This result suggests that an insertion product has likely formed at long irradiation times (> 6 hours), but it has yet to be isolated and characterized. It is important to realize that neither the green solid nor the toluene residues were washed, so presumably each fraction could contain a portion of the other fraction.

The CpCo(CO)₂ is likely present due to the residual toluene left on the solid; the toluene residue is primarily CpCo(CO)₂ as noted by its two strong absorbances at 2023 and 1960 cm⁻¹ in toluene. Further, a very large peak in the THF infrared spectrum of the green residue could be an anomaly or due to a compound such as (cyclopentadienyl)-2-5η-(2, 3, 4, 5-tetraphenyl)cyclopentadienone) cobalt (Figure 3.49), which was a product in the irradiation of CpCo(CO)₂ with diphenylacetylene and that has a reported v(CO) at 1990 cm⁻¹. Many different reactions could be occurring once CpCo(CO)₂ is formed in the photochemical reaction mixture. Much study has been done into the reactive intermediates of photolyzed CpCo(CO)₂, particularly the transient CpCo(CO)⁴³,⁹⁵ which reacts with
another CpCo(CO)$_2$ to form [CpCo(CO)]$_2$(μ-CO). This species was a suggested product in the reaction as mentioned above. Because [CpCo(CO)]$_2$(μ-CO) goes on to form Cp$_3$Co$_3$(CO)$_3$ in solution,$^{45}$ the assignment of [CpCo(CO)]$_2$(μ-CO) to the reaction mixture above is somewhat dubious in light of the absence of any evidence of forming Cp$_3$Co$_3$(CO)$_3$ (1670, 1760 cm$^{-1}$, toluene).$^{95}$ The photochemical and thermal reaction pathways of CpCo(CO)$_2$ are shown in Figure 3.50.

![Figure 3.49: Structure of (cyclopentadienyl)-2-5η-(2, 3, 4, 5-tetraphenyl) cyclopentadienone) cobalt.](image)

d. Diphenylacetylene

The reaction [CpCo(CO)]$_2$(μ-CH$_2$) with diphenylacetylene was run for only relatively short irradiation times, that is up to 80 minutes. At this point, the [CpCo(CO)]$_2$(μ-CH$_2$) $^1$H peaks remained predominant with only a few small other $^1$H peaks emerging just upfield of 4.64 ppm and, to a lesser extent, downfield of 7.5 ppm in C$_6$D$_6$. If the reactivity is like that of
Figure 3.50: Scheme of photochemical and thermal reaction pathways of CpCo(CO)$_2$.\textsuperscript{42,44}
phenylacetylene with \([\text{CpFe(CO)(\mu-CO)}]_2\), much longer irradiations would be necessary to see significant photoreactivity.

e. Dimethyl acetylenedicarboxylate

In contrast to the above alkynes, dimethylacetylene dicarboxylate undergoes facile reaction with \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\). The primary product is a single insertion product that is isolated nearly pure after column chromatography and subsequent sublimation. The \(^1\text{H}\) NMR spectrum of this product is shown in Figure 3.51. It displays a methylene \(^1\text{H}\) peak at 7.60, two Cp ring resonances at 4.74 and 4.66, and two resonances of the methyl groups of the DMAD at 3.68 and 3.27 ppm. The peak at 8.78 ppm is due to some impurity. Other than the 8.78 peak, these peaks are indicative of an insertion product in which DMAD is inserted between a carbonyl C atom and a Co atom. Two possible structures for this product are shown in Figure 3.52. The methylene protons remain in the methylene region rather than moving to the alkyl region. The insertion complex, \(\text{Cp}_2\text{Fe}_2(\text{CO})(\mu-\text{CO})\mu-\eta^1-\eta^3\text{C(CO}_2\text{Me})\text{C(CO}_2\text{Me})\text{CHCH}_3\), was reported by Knox et al. A crystal structure was obtained, which demonstrated insertion of DMAD between the hydrocarbyl C atom and Fe atom. Further, support of this structure was found in the \(^1\text{H}\) NMR in
Figure 3.51: $^1$H NMR spectrum of Cp$_2$Co$_2$(μ-CH$_2$)(μ-C(O)C$_2$R$_2$) (R = CO$_2$Me) in C$_6$D$_6$. 
C₆D₅CD₃ where the resonances of the product at 1.12 and -1.08 ppm correspond to an alkyl environment.²⁶

Figure 3.52: Possible structures of DMAD insertion product.

The structure involving the terminal carbene seems less likely to be the actual product although a similar species, [(CO)₅ReRe(CO)₄(=C(OMe)Ph)] has been reported.⁹⁸ The terminal carbene species shown in Figure 3.52 is similar to the proposed intermediate in cis-trans isomerization of alkylidene-bridged transition metal complexes where the alkylidene bridge is broken with subsequent formation of a terminal alkylidene complex (Figure 3.53).⁵ᵃ,²⁸,⁴⁰,⁹⁹ Because the rate of isomerization of alkylidene bridged systems is much slower than the rate for analogous carbonyl-bridged complexes, it has been suggested that the terminal alkylidene complex is presumably much higher in energy than the terminal carbonyl complexes.³³ The isomerization rate constant for [C₆ Fe(CO)]₂(μ-CO)(μ-CH₂) is about
Figure 3.53: Proposed cis-trans isomerization mechanism for alkylidene-bridged complexes.
five orders of magnitude smaller\textsuperscript{33} than that for [Cp\textsuperscript{*}Fe(CO)(\mu-CO)]\textsubscript{2}, which is 50 s\textsuperscript{-1} in cyclohexane at 297 K.\textsuperscript{13} This same trend is noted for the Cp complexes as well. Casey reported the half-life of trans-enriched [CpFe(CO)]\textsubscript{2}(\mu-CO)(\mu-CH\textsubscript{2}) to be 10 minutes at 36°C,\textsuperscript{40} which is much slower than that of [CpFe(CO)(\mu-CO)]\textsubscript{2}.\textsuperscript{100} Additionally, Altbach et al. also reported similar rate constant values for the cis/trans isomerization of [CpFe(CO)]\textsubscript{2}(\mu-CO)(\mu-CH\textsubscript{2}) in a variety of solvents. The rate of isomerization decreased with decreasing coordination ability of the solvent used (acetone > benzene > chloroform). Thus, they suggested that isomerization occurs through an intermediate involving a cleaved M-M bond and intact methylene bridge, which would be stabilized by coordinating solvents.\textsuperscript{99} The isomerization mechanism proposed by Altbach contrasts the proposed mechanism of Figure 3.53. These observations all lead to the conclusion that the terminal methylene complex is significantly higher in energy than the bridging isomer. Thus, we believe that the insertion product formed is more likely to remain bridged.

The IR spectrum (Figure 3.54) of the primary product (with a small amount of organic impurity) shows bands at 1708(s), 1686(s), and 1621(w-m) cm\textsuperscript{-1} in THF. This spectrum substantiates the suggested structure; the
Figure 3.54: Infrared spectrum of \( \text{Cp}_2\text{Co}_2(\mu-\text{CH}_2)(\mu-\text{C(}O\text{)}\text{C}_2\text{R}_2) \) (\( R = \text{CO}_2\text{Me} \)) with organic product in THF.
1708 and 1686 cm\(^{-1}\) bands are due to the bound DMAD carbonyls while the 1621 cm\(^{-1}\) band is due to the CO of insertion. The inserted CO group of \(\text{Cp}_2\text{Fe}_2(\mu\text{-CO})(\mu\text{-C(O)C}_2\text{R}_2)\), for \(\text{R} = \text{Ph}\), has a weak-medium CO stretch at 1731 cm\(^{-1}\) in \(\text{CH}_2\text{Cl}_2\), which is assigned to the CO of insertion.\(^{27}\)

The CO group band of \(\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_3\) in cyclohexane at 298 K is 1823 cm\(^{-1}\),\(^{15b}\) which corresponds to a shift of approximately 92 cm\(^{-1}\) upon insertion for the CO stretch. By analogy to \(\text{Cp}_2\text{Co}_2(\mu\text{-CO})(\mu\text{-CH}_2)\) and \(\text{Cp}_2\text{Co}_2(\mu\text{-CH}_2)(\mu\text{-C(O)C}_2\text{R}_2)\) (\(\text{R} = \text{CO}_2\text{Me}\)), the stretch of the inserted CO could be as low as 1718 cm\(^{-1}\). Precedence exists for even lower shifts in \(\nu(\text{CO})\), such as the 1601 cm\(^{-1}\) band in \(\text{CH}_2\text{Cl}_2\) assigned to the inserted CO in \([\text{CpW(CO)}_2]_2(\mu\text{-C(O)C}_2\text{R}_2)\), for \(\text{R} = \text{CO}_2\text{Me}\).\(^{101}\)

Finally, the mass spectrum of the organically impure product (Figure 3.55) showed a very low molecular weight species, corresponding to the organic entity, and a high molecular weight parent ion at 432 m/e. The latter would correspond to the expected mass of \(\text{Cp}_2\text{Co}_2(\mu\text{-CH}_2)(\mu\text{-C(O)C}_2\text{R}_2)\) (\(\text{R} = \text{CO}_2\text{Me}\)).

Preparing the DMAD insertion product with \([\text{CpCo(CO)}]_2(\mu\text{-CD}_2)\), followed by sublimation without heating, produced a sample of the
Figure 3.55: EI mass spectrum of Cp₂Co₂(μ-CH₂)(μ-C(O)C₂R₂)
(R = CO₂Me) and the organic product. a) Complete mass spectrum b) Region containing the M⁺.
insertion product whose $^1$H NMR spectrum contains the peak at 8.78 ppm in C$_6$D$_6$ (Figure 3.56). This peak provides evidence that the 7.6 ppm peak corresponds to the methylene protons while the 8.78 ppm peak does not. Column separation of the [CpCo(CO)$_2$(μ-CD$_2$)]$_2$ reaction mixture resulted in two bands, one red and one green. The red band has a 2D NMR (Figure 3.57) that shows a resonance at 6.94 ppm corresponding to the 6.91 ppm $^1$H resonance of [CpCo(CO)$_2$(μ-CH$_2$)]. The green band has a 2D resonance at 7.45 ppm, which corresponds reasonably with the 7.6 ppm $^1$H resonance of Cp$_2$Co$_2$(μ-CH$_2$)(μ-C(O)C$_2$R$_2$) (R = CO$_2$Me) (Figure 3.58). These spectra provide further evidence that the 7.6 ppm rather than the 8.78 ppm peak is a result of the CH$_2$ protons of Cp$_2$Co$_2$(μ-CH$_2$)(μ-C(O)C$_2$R$_2$) (R = CO$_2$Me). The purified organic compound, obtained through sublimation as well, showed a single $^1$H resonance at 1.34 ppm in C$_6$D$_6$, as shown in Figure 3.59.

Photochemical reaction of [CpCo(CO)$_2$(μ-$^{13}$CH$_2$)] and DMAD produced the same primary product, as demonstrated by peaks at 3.27, 3.68, 4.67, 4.74 ppm in the $^1$H NMR (Figure 3.60). The coupling between the $^{13}$C and methylene protons gives additional evidence that the 8.78 ppm band seen in Figure 3.51 is not due to Cp$_2$Co$_2$(μ-CH$_2$)(μ-C(O)C$_2$R$_2$) (R =
Figure 3.56: $^1$H NMR spectrum of $[\text{CpCo(CO)}]_2(\mu-\text{CD}_2)$ and DMAD reaction mixture in $\text{C}_6\text{D}_6$. 
Figure 3.57: ²D NMR spectrum in pentane of the first fraction of the column separation of the \([\text{CpCo(CO)}]_2(\mu-\text{CD}_2)\) and DMAD reaction mixture.
Figure 3.58: 2D NMR spectrum in pentane of the green fraction of the column separation of the \([\text{CpCo(CO)}]_2(\mu-\text{CD}_2)\) and DMAD reaction mixture.
Figure 3.59: ¹H NMR spectra in C₆D₆ of the organic product formed during the column chromatography separation of Cp₂Co₂(μ-CH₂)(μ-C(O)C₂R₂) (R = CO₂Me).
Figure 3.60: $^1$H NMR spectrum of the [CpCo(CO)]$_2$(μ-$^{13}$CH$_2$) and DMAD reaction mixture in C$_6$D$_6$ ($v = 250.133$ MHz).
The midpoints between the doublets at 7.29 and 7.90 ppm ($J^{13}\text{C}-\text{H}, 152 \text{ Hz}$) and 8.77 and 8.79 ($J^{13}\text{C}-\text{H}, 4.81 \text{ Hz}$) are 7.60 and 8.78 ppm, respectively, which corresponds well to Figure 3.51. However, the very different coupling constants make it clear that these two resonances are due to protons in different environments. The coupling of the 7.60 ppm doublet most closely resembles the coupling of $[\text{CpCo(CO)}]_2(\mu^{13}\text{CH}_2)$ ($J^{13}\text{C}-\text{H}, 144 \text{ Hz}$), as seen in Figure 3.61. Thus, the 7.60 ppm $^1\text{H}$ resonance is attributed to a methylene proton that maintains its bridging environment. The 8.78 ppm band is presumably due to some other compound present in the sample. Figure 3.60 also shows a small doublet at ca. 1.2 ppm, which may be due to another insertion product in which the DMAD inserts between the hydrocarbyl C and M atoms.

Another doublet at 10.83 ppm ($J^{13}\text{C}-\text{H}, 152 \text{ Hz}$) is also present in the reaction mixture. It may also correspond to a methylene proton. However, it is not attributed to $\text{Cp}_2\text{Co}_2(\mu-\text{CH}_2)(\mu-\text{C(O)C}_2\text{R}_2)$ ($R = \text{CO}_2\text{Me}$) because it is not only absent in the $^1\text{H}$ spectrum (Figure 3.60) but it is also present in a sample that, by NMR, does not contain $\text{Cp}_2\text{Co}_2(\mu-\text{CH}_2)(\mu-\text{C(O)C}_2\text{R}_2)$ ($R = \text{CO}_2\text{Me}$) (Figure 3.62).
Figure 3.61: $^1$H NMR spectrum of the \([\text{CpCo(CO)}]_2(\mu-^{13}\text{CH}_2)\) in $\text{C}_6\text{D}_6$ ($v = 250.133$ MHz).
Figure 3.62: $^1$H NMR spectrum of a fraction from the separation column of the [CpCo(CO)$_2$(μ-$^{13}$CH$_2$)] and DMAD reaction mixture in C$_6$D$_6$ ($v = 250.133$ MHz).
The $^{13}$C spectrum obtained after 5 hours of irradiation shows resonances at 104.0 ppm due to $[\text{CpCo(CO)}]_2(\mu-\text{CH}_2)^{5a}$ and 161.6, 122.6, 80.9, 58.4, 54.9, and 52.5 ppm due to other products of the photolysis (Figure 3.63). In additional experiments, the insertion product was initially observed via $^1$H NMR, but then disappeared. Both samples were chromatographed and $^{13}$C NMR spectra were obtained of the resultant fractions. None of the fractions contained the $^1$H resonances of the primary insertion product. In addition, only the first fraction contained any $^{13}$C resonances at all, and they were observed at 103.9(t), 148(d), and 161.6(d), 86(d), 57, 54, 51 ppm (Figure 3.64). Thus, by process of elimination between the two experimental $^{13}$C spectra, one can conclude that the $^{13}$C resonance at 122.6 ppm is likely the methylene carbon on the insertion product for $\text{Cp}_2\text{Co}_2(\mu-\text{CH}_2)(\mu-\text{C(O)C}_2\text{R}_2)$ ($\text{R} = \text{CO}_2\text{Me}$). In addition, no $^{13}$C resonances were observed between 250 and 400 ppm (Figure 3.63). This region is confined to terminal carbene carbon resonances. This observation suggests that the methylene bridge remains intact rather than forming a terminal carbene complex such as that shown in Figure 3.52. The proposed NMR assignments in C$_6$D$_6$ for $\text{Cp}_2\text{Co}_2(\mu-\text{CH}_2)(\mu-\text{C(O)C}_2\text{R}_2)$ ($\text{R} = \text{CO}_2\text{Me}$) are shown in Table 3.6.
Figure 3.63: $^{13}$C NMR Spectrum in C$_6$D$_6$ of the [CpCo(CO)]$_2$(μ-CH$_2$) and DMAD reaction mixture.
Figure 3.64: $^{13}$C NMR spectrum in C$_6$D$_6$ on of the separation column fractions of the [CpCo(CO)]$_2$(μ-CH$_2$) and DMAD reaction mixture.
Table 3.6: \(^1\text{H}\) and \(^{13}\text{C}\) Resonance Assignments in C\(_6\)D\(_6\) of Cp\(_2\)Co\(_2\)(\(\mu\)-CH\(_2\))(\(\mu\)-C(O)C\(_2\)R\(_2\)) (R = CO\(_2\)Me).

<table>
<thead>
<tr>
<th>Nuclei</th>
<th>Resonance</th>
<th>Coupling</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1\text{H})</td>
<td>3.27, 3.68 (Cp)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.67, 4.74 (Me)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.60 (CH(_2))</td>
<td>(J^{13}\text{C-H}) 152 Hz</td>
</tr>
<tr>
<td>(^{13}\text{C})</td>
<td>122.6 (CH(_2))</td>
<td></td>
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</table>

The mechanism proposed for this reaction is shown in Figure 3.65. Bursten et al. have studied the reactions of [CpFe(CO)(\(\mu\)-CO)]\(_2\) with alkynes by using LFP kinetic methods. They concluded that the reaction is associative bimolecular with rate constants on the order of \(10^4\) M\(^{-1}\)s\(^{-1}\). In this mechanism, the alkyne first binds to the CO-loss species in an \(\eta^2\) fashion, followed immediately by rearrangement into the inserted geometry.\(^{23}\) Similarly, it appears that [CpCo(CO)]\(_2\)(\(\mu\)-CH\(_2\)) undergoes photochemical reactivity that is attributed to the formation of a CO-loss product.

Attempts to grow a single crystal of Cp\(_2\)Co\(_2\)(\(\mu\)-CH\(_2\))(\(\mu\)-C(O)C\(_2\)R\(_2\)) (R = CO\(_2\)Me) in pentane at -35°C have resulted in dark crystals that disappear upon solvent warming. Attempts continue to isolate the species. A crystal structure would definitively determine the structure of this species. This result would be important due to the unprecedented structure proposed here. As noted in the introduction, no synthetic studies
Figure 3.65: Proposed reaction mechanism of the formation of \( \text{Cp}_2\text{Co}_2(\mu-\text{CH}_2)(\mu-\text{C(O)C}_2\text{R}_2) \) (\( R = \text{CO}_2\text{Me} \)).
on the reaction of alkylidene-bridged species have been reported which suggest formation of any insertion between the carbonyl carbon and metal atoms.26

The alternative insertion product reported here is very exciting. It is possible that the number of CO bridges plays a role in this alternative insertion among other possibilities, the nature of the metal and alkyl bridging groups. As shown in Figure 1.13, the CO-loss complex of the ethylidene-bridged species, \([\text{CpFe}]_2(\mu\text{-CO})_2(\mu\text{-CHCH}_3)\), contains two bridging CO groups; thus, upon \(\eta^2\) ligation of the alkyne, both a CHCH\(_3\) and CO bridge are still intact. However, the CO-loss species of \([\text{CpCo(CO)}]_2(\mu\text{-CH}_2)\), \([\text{CpCo}]_2(\mu\text{-CO})(\text{CH}_2)\), contains only one bridging CO group; thus, upon \(\eta^2\) ligation of the alkyne, the remaining CO bridge is disrupted leaving only a CH\(_2\) bridge. It is possible that in order to maintain the dinuclear framework, the methylene bridge preferentially remains intact, providing additional stability to the complex while the CO group is free to interact with the alkyne.

f. Solid State NMR: Charge on the Methylene Carbon

As stated above, \([\text{CpCo}]_2(\mu\text{-CO})(\mu\text{-CH}_2)\) demonstrates unique reactivity with DMAD forming \(\text{Cp}_2\text{Co}_2(\mu\text{-CH}_2)(\mu\text{-C(O)C}_2\text{R}_2)\) (R = CO\(_2\text{Me}\)) with insertion between a CO carbon and Co atom which contrasts other
Therefore, it is interesting to consider if the charge on the hydrocarbyl carbon plays a role in these reactions.

The charge on the methylene carbon atoms of dinuclear compounds have been obtained by a variety of methods. The C\textsubscript{1s} binding energy found by PES is indicative of a -0.5 e charge.\textsuperscript{7} This value is in agreement with the interpretation of \textsuperscript{13}C chemical shifts of these compounds, which suggest a partial negative charge on the carbon atom.\textsuperscript{3a} However, a high-resolution X-ray diffraction electron density map of [CpMn(CO)\textsubscript{2}]\textsubscript{2}(\textmu\text{-}CH\textsubscript{2}) indicates no excess charge buildup.\textsuperscript{8} This result is in accord with the solid state \textsuperscript{2}D NMR of \textit{cis}-[Cp\textsuperscript{d}Fe(CO)]\textsubscript{2}(\textmu\text{-}CO)(\textmu\text{-}CD\textsubscript{2}) (Cp\textsuperscript{d} = 5\% deuterated Cp), which suggests the absence of excess negative charge on the methylene-bridge carbon atom.\textsuperscript{103} This value is calculated from the quadrupole coupling constant that is obtained from the spectrum. Although the extensive calculations were not performed in this study, an important first step was taken in the attainment of the solid state \textsuperscript{2}D NMR of [CpCo(CO)]\textsubscript{2}(\textmu\text{-}CD\textsubscript{2}). The quadrupole coupling constant was found to be 177 kHz (Figures 3.66 and 3.67). Calculations of this type may prove useful in designing alkylidene bridge complexes that selectively bridge
Figure 3.66: Solid state static $^2$H NMR spectra of $\text{[CpCo(CO)]}_2(\mu$-$\text{CD}_2$). The model fit to the data (-----) and the actual data (------) ($v = 61.482$ Hz).
Figure 3.67: Solid state MAS $^2$H NMR spectra of $[\text{CpCo(CO)}]_2(\mu\text{-CD}_2)$. a) Spectrum of the model fit of the data  b) Spectrum of the actual data acquired.
solely through the hydrocarbyl-bridged carbon atom rather than the carbonyl-carbon atom.

2. Phosphorus-Containing Compounds and [CpCo(CO)]₂(μ-CH₂)

Attempts were made to observe photochemical substitution chemistry of [CpCo(CO)]₂(μ-CH₂) with PMe₃, PPh₃, and P(OMe)₃. The ethylidene-bridged complex [CpFe(CO)]₂(μ-CO)(μ-CHCH₃) has been shown to form dinuclear monosubstituted products upon irradiation in the presence of phosphorus-containing compounds. Since Kao et al.³⁴ first reported Cp(CO)Fe(μ-CO)(μ-CHCH₃)Fe[P(n-Bu)₃]Cp (Figure 3.68), other monosubstituted analogs of this ethylidene-bridged complex with PMe₃, PPh₃ and P(OPh)₃ have been isolated.²² The studies reported here are the preliminary experiments to determine if [CpCo(CO)]₂(μ-CH₂) reacts with PMe₃, P(OMe)₃, and PPh₃ under photolytic conditions to form Cp(CO)Co(μ-CO)(μ-CH₂)Co(L) (L=PMe₃, P(OMe)₃, PPh₃). Because these monosubstituted complexes have been shown to form through reaction with a CO-loss dinuclear intermediate,²² these reactions would be additional evidence for the importance of the CO-loss photochemical process of [CpCo(CO)]₂(μ-CH₂).
Figure 3.68: Cp(CO)Fe(μ-CO)(μ-CHCH₃)Fe[P(n-Bu)₃]Cp.

a. PMe₃

It was not possible to define the photochemical reaction of [CpCo(CO)]₂(μ-CH₂) with PMe₃ because of a facile thermal reaction. The solution changed from red to yellow within 6 hours. The IR band at 1930 cm⁻¹ in hexane suggests the possibility of the formation of CpCo(CO)PMe₃, which has an IR band in pentane at 1923 cm⁻¹. The monosubstituted dinuclear product, Cp(CO)Co(μ-CO)(μ-CH₂)Co(PMe₃)Cp, would be expected to have another CO band in the bridging region. The yellow solution noted in this reaction could correspond to the orange-red color of CpCo(CO)PMe₃. However, the NMR data does not correspond as well with the previously reported values of CpCo(CO)PMe₃, which are δ 4.35 (d) and 0.93 (d) in C₆D₆. The reaction of [CpCo(CO)]₂(μ-CH₂) with PMe₃ was performed in toluene, which was removed via vacuum before dissolution into C₆D₆. The compound seemed to be pulled off with the toluene with only a residual amount left for NMR analysis; thus, with only a small
amount of the material left for NMR analysis, most of the signals were very weak. The only possible correlation is the multiplet is seen at 0.9 ppm, which seems to correspond to the doublet noted at 0.93 ppm in the literature.\textsuperscript{104}

Another known PMe\textsubscript{3} containing monomer of Co, CpCo(PMe\textsubscript{3})\textsubscript{2}, is produced at low temperature from CoCl(PMe\textsubscript{3})\textsubscript{3} and LiC\textsubscript{5}H\textsubscript{5}.\textsuperscript{105} In that report, there is a small PH coupling of the Cp proton, ($\delta$ 4.51 ppm, t, $J$(PH) 1.4 Hz). We do not observe this coupling in the $^1$H NMR spectra of the photoproducts. Although CpCo(PMe\textsubscript{3})\textsubscript{2} seems unlikely to be one of the thermal products, the presence of multiple peaks in the NMR make it clear that there are multiple products in the reaction. No compounds have yet been isolated.

b. PPh\textsubscript{3}

Triphenylphosphine shows no thermal reaction with [CpCo(CO)]\textsubscript{2}(\mu-CH\textsubscript{2}) after 220 minutes via NMR. When the photochemical experiment is carried out in an NMR tube, little reactivity was noted with only small peaks appearing in the baseline after 30 minutes of irradiation. However, when the experiments were carried out in Schlenk flasks and followed by IR, within 30 minutes all starting material is consumed with only small
peaks at 2023 and 1927 cm⁻¹ remaining in toluene. These two bands do not appear to be due to the same species because at 60 minutes the 1927 cm⁻¹ band continues to grow, while the 2022 cm⁻¹ band appears not to change in intensity. These results are not consistent with \([\text{Cp(CO)Co(μ-CO)(μ-CH}_2\text{)Co(PPh}_3\text{)}\text{Cp}]\) because no bridging CO band is observed in the IR spectrum. After an additional 30 minutes irradiation, the solution turns pale purple and no CO bands are observable, suggesting complete decomposition of the CO containing species.

c. \(\text{P(OMe)}_3\)

Trimethylphosphite showed little thermal reactivity compared to the photochemical reactivity over the same time frame. After as little as 5 minutes of irradiation, the color changed from red to an amber color and nearly all of the starting material was consumed. There are many doublets in the Cp and the \(\text{P(OMe)}_3\) regions of the \(^1\text{H}\) spectrum and a doublet at 6.77 ppm, which could be evidence for a methylene group (Figure 3.69). The NMR spectra thus demonstrate the possibility of the formation of \(\text{Cp(CO)Co(μ-CO)(μ-CH}_2\text{)Co[P(OMe)}_3\text{)Cp}\). Because the IR spectra were obtained after the solution was exposed to air (1965 and 1947 cm⁻¹, hexane) or the next day (1948 and 1938 cm⁻¹, \(\text{C}_6\text{D}_6\)), they do not provide confirmation of the NMR results.
Figure 3.69: $^1$H NMR spectrum of the reaction mixture of [CpCo(CO)]$_2$(μ-CH$_2$), 6.91 and 4.64 ppm, and P(OMe)$_3$, 3.25(d), after 6 minutes of irradiation in C$_6$D$_6$. 
The suggestion that \( \text{P(OMe)}_3 \) may form a monosubstituted complex such as \( \text{Cp(CO)}\text{Co(\(\mu\)-\(\text{CO}\))(\(\mu\)-\(\text{CH}_2\))Co[\text{P(OMe)}_3]}\text{Cp} \), while \( \text{PPh}_3 \) appears not to form \( \text{Cp(CO)}\text{Co(\(\mu\)-\(\text{CO}\))(\(\mu\)-\(\text{CH}_2\))Co(\text{PPh}_3]}\text{Cp} \) is interesting in light of recent time-resolved infrared spectroscopy studies.\(^{18}\) The formation of disubstituted phosphite complexes such as \( [\text{CpFe(\(\mu\)-\(\text{CO}\))[\text{P(OMe)}_3]}]_2 \) through a radical substitution pathway have been observed, while phosphines were not observed to form analogous disubstituted complexes. The decreased basicity of the phosphite versus phosphine ligands may play some role in these reactions.

By analogy to the \( \text{PMMe}_3 \) discussion above, the possible formation of two known monomers was considered, \( \text{CpCo(CO)}\text{P(OMe)}_3 \) and \( \text{CpCo[}\text{P(OMe)}_3]_2 \). Because of the large number of doublets observed in the reaction mixture spectrum, the NMR values of the monomers are difficult to compare to those of the reaction mixture. The former complex, \( \text{CpCo(CO)}\text{P(OMe)}_3 \), has a CO stretch in THF at 1946 cm\(^{-1}\) and two NMR resonances in \( \text{C}_6\text{D}_6 \) (\( \delta \) 4.91, d, \( J(\text{PH}) \) 0.7 Hz; 3.53, d, \( J(\text{PH}) \) 12.3 Hz).\(^{106}\) The latter complex, \( \text{CpCo[}\text{P(OMe)}_3]_2 \), has no CO stretching bands and two \(^1\text{H} \) NMR resonances (\( \delta \) 4.63, s; 3.48, virtual triplet) in \( \text{d}_6\)-acetone.\(^{105}\) The apparent couplings observed for the photoproducts were on the order of 7
to 15 Hz for the Cp region (ca. 4-5 ppm) and 5 to 15 Hz for the P(OMe)₃ region (ca. 3-4 ppm). The Cp region couplings do not compare well to the 0.7 Hz observed in the literature for CpCo(CO)[P(OMe)₃]. Because the ¹H NMR values for CpCo[P(OMe)₃]₂ are reported in d₆-acetone, comparison is dubious at best. The 4.63 (s) peak would be difficult to distinguish from residual [CpCo(CO)]₂(μ-CH₂), while there are many peaks in the vicinity of 3.48 ppm.

Obviously, interesting photochemistry has occurred in this case. Future separations should prove fruitful in finding multiple photoproducts, including perhaps Cp(CO)Co(μ-CO)(μ-CH₂)Co[P(OMe)₃]Cp. These spectroscopic data obtained could be consistent with a monosubstituted dinuclear complex, Cp(CO)Co(μ-CH₂)Co[P(OMe)₃]Cp, which would be expected to have a single ν(CO) band and ¹H NMR resonances in the methylene, the Cp, and the P(OMe)₃ regions.

3. Kinetic Studies of [CpCo(CO)]₂(μ-CH₂) with 2 Electron Donors

Because the CO-loss intermediate is formed upon photolysis of [CpCo(CO)]₂(μ-CH₂), it is expected to react readily with 2 electron donors such as CO, phosphines and phosphites. It was shown previously that the CO-loss species is the intermediate in the formation of phosphine and
alkyne substitution in numerous dinuclear organometallic compounds.\textsuperscript{22} Figure 1.10 shows this reaction mechanism proposed for the substitution of phosphines and phosphites. Thus, the lack of photoreactivity of [CpCo(CO)]\textsubscript{2}(\mu-CH\textsubscript{2}) with PPh\textsubscript{3} and diphenylacetylene is surprising.

Laser flash photolysis was used to follow the reactions of [CpCo]\textsubscript{2}(\mu-CO)(\mu-CH\textsubscript{2}) with P(OMe)\textsubscript{3} and PMe\textsubscript{3}. With these two ligands, reaction was observed. The value of \(k_Q\), the second order rate constant for the reaction of [CpCo]\textsubscript{2}(\mu-CO)(\mu-CH\textsubscript{2}) with P(OMe)\textsubscript{3} and PMe\textsubscript{3}, calculated by a plot of \(k_{\text{obs}}\), the pseudo-first-order rate constant of the disappearance of the CO-loss intermediate, versus [quencher] in both reactions was found to be of the order of 10\textsuperscript{6} M\textsuperscript{-1}s\textsuperscript{-1}. These values correspond well to similar photoreaction studies of [CpFe(CO)]\textsubscript{2}(\mu-CO)(\mu-CHCH\textsubscript{3}) with the same or similar 2 electron donors. The second order rate constants of the reaction of [CpFe]\textsubscript{2}(\mu-CO)\textsubscript{2}(\mu-CHCH\textsubscript{3}) with P(OPh)\textsubscript{3} and PMe\textsubscript{3} in toluene are (7.5 ± 0.6) \times 10\textsuperscript{5} M\textsuperscript{-1}s\textsuperscript{-1} and > 10\textsuperscript{8} M\textsuperscript{-1}s\textsuperscript{-1}, respectively.\textsuperscript{22} This data suggest that the steric constraints of the CO-loss product influence the size selectivity of these substitution reactions. [CpFe]\textsubscript{2}(\mu-CO)(\mu-CH\textsubscript{2}), which has three bridges, shows selectivity between P(OPh)\textsubscript{3} and PMe\textsubscript{3}, with the smaller
phosphine (PMe$_3$) adding at a faster rate. On the other hand, [CpCo]$_2$(μ-CO)(μ-CH$_2$), which has only two bridges, showed no selectivity between P(OMe)$_3$ and PMe$_3$, adding both at about the same rate.

Reaction of the CO-loss product of [Cp*Fe(CO)]$_2$(μ-CO)(μ-CH$_2$), [Cp*Fe]$_2$(μ-CO)$_2$(μ-CH$_2$), with CO in a saturated cyclohexane solution has a $k_Q$ of the order of 10$^7$ M$^{-1}$s$^{-1}$. The second order rate constant of the reaction in toluene of [CpFe]$_2$(μ-CO)$_2$(μ-CHCH$_3$) and CO is (3.4 ± 0.4) x 10$^6$ M$^{-1}$s$^{-1}$ which is about an order or magnitude lower than observed for the reaction of [Cp*Fe]$_2$(μ-CO)$_2$(μ-CH$_2$) with CO in this study, indicating that the added steric constraint due to the ethylidene bridge influences the association rate.

Comparisons of the $k_Q$ values of this study with those of previous studies are extremely tenuous due to the lack of reliability of the data obtained in this study. The reactions could only be monitored for less than 20 μs due to instrumental constraints. This time period would have been sufficient in the PMe$_3$ and P(OMe)$_3$ reactions where their half-lives are on the order of 2 μs except that an even shorter time was followed (ca. 2 μs). McKee$^{77}$ followed the decays of [CpFe]$_2$(μ-CO)$_3$ for about 1 ms, over 2 orders of magnitude longer than this study allowed. The photoreactions of
[CpCo(CO)]$_2$(μ-CH$_2$) with other 2 electron donors like phenylacetylene and 1-hexyne were so slow that only a fraction of their half-lives could be followed in 20 μs. The only reaction kinetics reported above that are based on even 1 half-life are the reactions of [CpCo(CO)]$_2$(μ-CH$_2$) with P(OMe)$_3$ and PMe$_3$, $t_{1/2} = 2$ μs.

The results presented here should be viewed as a starting point for additional studies. These studies should focus on P(OMe)$_3$. It does not undergo thermal reaction with [CpCo(CO)]$_2$(μ-CH$_2$) and its photoreaction can be monitored for multiple half-lives.

4. Solution Photochemistry of [CpMn(CO)$_2$(μ-CH$_2$)]

As noted earlier, [CpMn(CO)$_2$(μ-CH$_2$)] definitively undergoes CO-loss at low temperature, but the transient absorption spectrum cannot confirm the existence of the CO-loss product at room temperature. The solution reactions of [CpMn(CO)$_2$(μ-CH$_2$)] with alkynes, phosphines, and phosphites could therefore provide additional insight into whether the CO-loss product, [CpMn(CO)$_2$(μ-CO)(μ-CH$_2$)], is formed at room temperature or not. If photochemical reaction with phosphines or phosphites results in mono-substitution products or if reaction with alkynes result in insertion products, this would indicate the likely formation of a CO-loss
intermediate, as based on the proposed mechanism\textsuperscript{22} of photosubstitution reactions of this type. Further, because of the existence of multiple CO-loss species in the low temperature matrix, disubstitution complexes may also be possible. These solution studies, however, suggest these reactions may be more problematic than those of \([\text{CpCo(CO)}_2(\mu-\text{CH}_2)]\) due to the greater tendency of \([\text{CpMn(CO)}_2_2(\mu-\text{CH}_2)]\) toward photodecomposition.

a. Irradiation in the Absence of Other Reactants

While \([\text{CpCo(CO)}_2(\mu-\text{CH}_2)]\) is stable under irradiation in the absence of other reactants, \([\text{CpMn(CO)}_2_2(\mu-\text{CH}_2)]\) appears to be photosensitive. Irradiation of \([\text{CpMn(CO)}_2_2(\mu-\text{CH}_2)]\) at room temperature leads to its partial decomposition. The resulting IR peaks of the irradiated solution are 2175 (broad, m), 2017(w), 1976(w), 1882 (broad, w), and \(-1675\) (vvs, probably artifact) cm\(^{-1}\). The \(v(\text{CO})\) bands of \([\text{CpMn(CO)}_2_2(\mu-\text{CH}_2)]\) are at 1977(w), 1947(vs), 1917(s), and 1901(w) cm\(^{-1}\) while those of \(\text{CpMn(CO)}_3\) are 2028 and 1946 cm\(^{-1}\) in 90\% MCH/10\% 3MP solution. Therefore, the observation that upon irradiating a \([\text{CpMn(CO)}_2_2(\mu-\text{CH}_2)]\) solution the 1948 cm\(^{-1}\) peak increases in intensity while shifting to 1945 cm\(^{-1}\) while the 1917 cm\(^{-1}\) peak decreases coupled with an increase of the 2028 cm\(^{-1}\) peak
suggests that [CpMn(CO)₂]₂(μ-CH₂) is partially consumed while CpMn(CO)₃ is formed.

Low temperature irradiation yields evidence for the complete loss of [CpMn(CO)₂]₂(μ-CH₂). An NMR tube sample was frozen in liquid nitrogen and then twirled for 5 minutes in front of a UV lamp with one refreezing. The sample was then immediately placed in the NMR and the temperature was subsequently lowered for NMR spectral analysis. Figure 3.70 shows the NMR spectra at 173 K before (δ 8.62(d); 4.58(t) ppm) and after photolysis in d₁₄-methylcyclohexane. Note that the spectrum after photolysis is much broader and indicates the presence of residual solvent protons only. A brown precipitate was noted in the solution, indicating decomposition of the sample.

Multiple laser pulses with the 308 nm laser also indicate a decrease in absorbance due to the decomposition of [CpMn(CO)₂]₂(μ-CH₂). In this case a brown-orange precipitate was noted.

b. Irradiation in the Presence of Dimethyl acetylenedicarboxylate

Attempts to react [CpMn(CO)₂]₂(μ-CH₂) with DMAD resulted in the formation of a yellow solution with a fine orange precipitate. Only a very small peak was noted in the C₆D₆ ¹H NMR at 5.15 ppm. Extraction with CD₃CN yielded a yellow solution with a ¹H NMR peak at 4.68 ppm in
Figure 3.70: $^1$H NMR spectrum of $[\text{CpMn(CO)}_2]_2(\mu-\text{CH}_2)$ in d$_{14}$MCH at 173 K. a) Before irradiation  b) After irradiation.
CD$_3$CN. This $^1$H resonance does not match that of CpMn(CO)$_2$, whose $^1$H NMR has a single peak at 4.88 ppm in CD$_3$CN. The solution shows \textit{v}(CO) bands in THF at 1979(w), 1939(s), 1909(m), 1895(sh), 1868(w) while the remaining orange solid was dissolved in THF and showed the following \textit{v}(CO) bands: 2261(m), 2113(w), 1938(w), 1909(w), 1868(w) and 1738 (w, probably atmospheric water) cm$^{-1}$. Both IR spectra were weak and noisy; however, comparing the two suggests that the 1939 and 1909 cm$^{-1}$ resonances may be due to the same species in that they both show the same trend in relative intensities between the two spectra.

All of these solution experiments were done at an extremely small scale (1-2 mg). Thus, future investigations invoking larger sample sizes may yield sufficient material to analyze more fully.

C. Probing for Potential Radical Formation

As demonstrated in the previous sections, both [CpCo(CO)$_2$($\mu$-CH$_2$)] and [CpMn(CO)$_2$($\mu$-CH$_2$)] faciley form CO-loss species upon photolysis. The CO-loss species [CpCo]$_2$(\micro-CO)(\micro-\text{CH$_2$C$_2$R$_2$}) (R = CO$_2$Me). However, the question still remains as to whether these
complexes undergo photochemically induced homolytic cleavage of the M-M bond to form either radicals or potentially short-lived diradical species.

While the mononuclear radical CpFe(CO)$_2^*$ has been observed upon the photolysis of [CpFe(CO)(μ-CO)]$_2$ through a variety of transient spectroscopies, similar experiments using UV-vis detection have not yielded evidence of radical species formation from [CpFe(CO)]$_2$(μ-CO)(μ-CHCH$_3$). Presumably, the resultant mononuclear radical fragment Cp(CO)(CHCH$_3$)Fe* would be unstable and likely energetically inaccessible. From the analogy of [CpFe(CO)]$_2$(μ-CO)(μ-CHCH$_3$), the formation of mononuclear radical fragments from [CpCo(CO)]$_2$(μ-CH$_2$) seems unlikely because the resultant mononuclear fragments would be CpCo(CO)* and CpCo(CO)(=CH$_2$). In addition, [CpFe(CO)]$_2$(μ-CO)(μ-C=CH$_2$) does not form Cp(CO)(C=CH$_2$)Fe* upon photolysis or treatment with tetracyanoethylene. Thus, it appears that preference of the alkylidene ligand to form bridged rather than terminal species is responsible for the M$_2$(μ-CR$_2$) unit remaining intact through photolysis. This suggests that compounds such as [CpCo(CO)]$_2$(μ-CH$_2$) and
[CpMn(CO)\textsubscript{2}]_2(\mu-\text{CH}_2)\) will not undergo homolytic cleavage into two mononuclear fragments.

The potential formation of a 1,3-diradical as related to the dimetallacyclopropane\textsuperscript{9} nature of \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) and \([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\) was discussed in the introduction. Extending the analogy of cyclopropane-to-propylene isomerization suggests the possible formation of a metal-carbonyl carbon based 1, 3 diradical, which, could subsequently rearranges to form a terminal carbene complex (Figure 3.71A). Other than the terminal heteroatom carbene complex of Fischer, \([\text{(CO)}_5\text{ReRe(CO)}_4(=\text{C(OMe)Ph})]\), which does not contain cyclopentadienyl ligands, few other dinuclear terminal carbene complexes\textsuperscript{108} of this nature have been reported. Thus, isolation of such species seems unlikely, but at very short times, they may be spectroscopically observable.

The formation of a metal based 1,3-diradical is also reasonable (Figure 3.71). These species would not be observed in a low temperature hydrocarbon matrix due to fast recombination under the conditions of a low temperature, viscous,\textsuperscript{109} rigid solution, which inhibits molecule mobility of large fragments resulting in a "cage effect". Even complexes that are known to undergo photochemical homolytic cleavage into
Figure 3.71: Scheme of possible photochemical 1,3-diradical formation of \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\).
mononuclear radicals, such as Mn$_2$(CO)$_{10}$, the mononuclear radicals are not observed under such conditions.$^{74}$

As stated before, in solution, [CpFe(CO)(μ-CO)$_2$]$_2$ like Mn$_2$(CO)$_{10}$ undergo homolytic cleavage while the asymmetrically bridged [CpFe(CO)$_2$(μ-CO)(μ-CHCH$_3$)] does not.$^{10a,22}$ By analogy to [CpFe(CO)$_2$(μ-CO)(μ-CHCH$_3$)], [CpCo(CO)$_2$(μ-CH$_2$)], which is asymmetrically bridged with one bridging (μ-CH$_2$), would not be expected to undergo homolytic cleavage into two mononuclear radicals. However, [CpCo(CO)$_2$(μ-CH$_2$)] is only singly bridged rather than doubly bridged, like [CpFe(CO)$_2$(μ-CO)(μ-CHCH$_3$)]. Therefore, there may be additional flexibility in the M$_2$(μ-CH$_2$) framework of [CpCo(CO)$_2$(μ-CH$_2$)] that upon homolytic M-M bond cleavage, the respective M-Cp(CO)$_n$ sides of the molecule might swing apart allowing the lifetime of such a species in solution to increase such that it might be observable.

A. Transient Absorption Spectroscopy

The transient absorption spectra of [CpCo(CO)$_2$(μ-CH$_2$)], Figure 3.19, [CpMn(CO)$_2$(μ-CH$_2$)], Figure 3.35, and [Cp*Fe(CO)$_2$(μ-CO)(μ-CH$_2$)], Figure 3.46, give no indication of any short-lived species, only the relatively long lived CO-loss species previously discussed. The only peaks
present decay at the same rate and are long-lived, seconds rather than microseconds. It should be noted that the ΔA observed in the transient spectrum of [CpMn(CO)₂]₂(μ-CH₂) are sufficiently weak that identification of even the CO-loss species is tenuous at best.

The spectra of [Cp*Fe(CO)]₂(μ-CO)(μ-CH₂) and [CpCo(CO)]₂(μ-CH₂) indicate that they behave analogously to [CpFe(CO)]₂(μ-CO)(μ-CHCH₃) in that no complexes other than the respective CO-loss species are observed within 1.4, 1.4, and 3 μs,²² respectively, after the laser flash. [•(OC)₄ReL°LRe(CO)₄•] (L= among others, dppp), a known photochemically produced organometallic diradical, has a lifetime of 36 ns.³⁷ It may therefore be that any diradical species forms and recombines by the time the spectrum is obtained (1.4 μs) or that the species formed does not have a sufficiently different absorption profile to be observed through a Δ absorption spectrum.

The lack of formation of a photochemical radical species from [Cp*Fe(CO)]₂(μ-CO)(μ-CH₂) and [CpCo(CO)]₂(μ-CH₂) is also evident from the shape of the absorbance trace in the LFP experiments. Figure 3.72 shows the absorption traces for the maxima of the CO-loss products of [CpCo(CO)]₂(μ-CH₂), [Cp*Fe(CO)]₂(μ-CO)(μ-CH₂), and [CpFe(CO)(μ-CO)]₂. In each case, there is an abrupt increase in the absorption just after the
Figure 3.72: LFP absorption traces of [CpCo(CO)]$_2$(μ-CH$_2$) (— — —) ($\lambda$ = 550 nm),
[CpFe(CO)(μ-CO)]$_2$ (· · · · · ·) ($\lambda$ = 515 nm), and [Cp*Fe(CO)]$_2$(μ-CO)(μ-CH$_2$)
(———-)(λ = 490 nm). [Excitation $\lambda$ = 308 nm]
flash. These traces represent the formation of the CO-loss species

\[ \text{[CpCo]}_2(\mu-\text{CO})(\mu-\text{CH}_2) \ (\lambda, \ 550 \ \text{nm}), \ \text{[Cp}^*\text{Fe]}_2(\mu-\text{CO})_2(\mu-\text{CH}_2) \ (\lambda, \ 490 \ \text{nm}), \]

and \[ \text{[CpFe]}_2(\mu-\text{CO})_3 \ (\lambda, \ 515 \ \text{nm}), \] which absorb more strongly at their respective wavelengths than do their parent complexes (Figures 3.18 and 3.47, and Figure 1 of reference 16).

In Figure 3.73, the LFP traces in Figure 3.72 are overlaid. There are evident differences between the trace of \[ \text{[CpFe}}(\text{CO})(\mu-\text{CO})]_2, \] which forms mononuclear radicals,\textsuperscript{14} and the traces of \[ \text{[Cp}^*\text{Fe}(\text{CO})]_2(\mu-\text{CO})(\mu-\text{CH}_2) \] and \[ \text{[CpCo}(\text{CO})]_2(\mu-\text{CH}_2), \] which do not form radical species.\textsuperscript{22} For both \[ \text{[Cp}^*\text{Fe}(\text{CO})]_2(\mu-\text{CO})(\mu-\text{CH}_2) \] and \[ \text{[CpCo}(\text{CO})]_2(\mu-\text{CH}_2), \] the initial abrupt increase in absorption is followed by a slow decline in absorbance. The slow decline in the intensity of the CO-loss species is due to their reaction with free CO to reform their respective parent compounds, which have a lower absorbance at the monitoring wavelength. This process is represented in Figures 3.74 and 3.75.

The trace for \[ \text{[CpFe}(\text{CO})(\mu-\text{CO})]_2 \] shows the same abrupt rise upon initial formation of \[ \text{[CpFe]}_2(\mu-\text{CO})_3, \] the CO-loss product. Unlike the two CH\textsubscript{2}-bridged complexes, however, the initial rise is followed by a steady increase in the absorption trace. This rise is an indication of the
Figure 3.73: Overlaid LFP Absorption Traces of the CO-loss products from \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) (---), \([\text{CpFe(CO)(µ-CO)}]_2\) (...........), and \([\text{Cp*Fe(CO)}]_2(µ-CO)(µ-\text{CH}_2)\) (-----).
Figure 3.74: Scheme of observed solution photochemical and thermal reactivity of \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\).
Figure 3.75: Scheme of observed solution photochemical and thermal reactivity of \([\text{Cp}^*\text{Fe}(\text{CO})]_2(\mu-\text{CO})(\mu-\text{CH}_2)\).
simultaneous formation of long-lived $[\text{CpFe}]_2(\mu-\text{CO})_3$ ($t_{1/2}$ ca. 3 s)$^{14,15b,16}$ and short-lived $\text{CpFe}(	ext{CO})_2^*$ ($t_{1/2}$ ca. 25 $\mu$s).$^{13,14}$ The initial absorption rise is less abrupt because $\text{CpFe}(	ext{CO})_2^*$ absorbs less strongly than either $[\text{CpFe}(\text{CO})(\mu-\text{CO})]_2$ or $[\text{CpFe}]_2(\mu-\text{CO})_3$ at the monitoring wavelength; consequently, as this short-lived radical recombines to form $[\text{CpFe}(\text{CO})(\mu-\text{CO})]_2$, the absorption increases. Thus, the radical is already recombining during the initial rise to form $[\text{CpFe}(\text{CO})(\mu-\text{CO})]_2$. The trace continues to increase rather than gradually decrease because the increase in absorbance at 515 nm (monitoring $\lambda$) due to the recombination of $\text{Cp(CO)}_2^*\text{Fe}^*$ is greater than the decrease in the absorbance due to the recombination of CO with $[\text{CpFe}]_2(\mu-\text{CO})_3$ (Figure 3.76). Thus, the traces also suggest that $[\text{CpCo}(\text{CO})]_2(\mu-\text{CH}_2)$ and of $[\text{Cp}^*\text{Fe}(\text{CO})]_2(\mu-\text{CO})(\mu-\text{CH}_2)$ do not form radicals that are observable at the $\mu$s time scale. The trace of $[\text{CpMn}(\text{CO})_2]_2(\mu-\text{CH}_2)$ could not be obtained due to the negligible positive $\Delta\lambda$ in the transient spectrum (Figure 3.35).

B. ESR

A method of directly observing radical species is ESR. The ESR spectrum of $[\text{CpCo}(\text{CO})]_2(\mu-\text{CH}_2)$ obtained during continuous photolysis in 3MP does not show a radical signal (Figure 3.77), suggesting again that $[\text{CpCo}(\text{CO})]_2(\mu-\text{CH}_2)$ does not form radical species, either mononuclear or
Figure 3.76: Scheme of observed solution photochemical and thermal reactivity of [CpFe(CO)(μ-CO)]$_2$. 
Figure 3.77: ESR spectrum of $[\text{CpCo(CO)}]_2(\mu-\text{CH}_2)$ obtained during photolysis in 3MP at ambient temperature.
dinuclear, upon photolysis. The spectrum is obtained during photolysis, because the potential diradical species would be expected to have a very short lifetime (ca. 100 ns).\textsuperscript{37}

C. Solution Reactivity with Halocarbons

The photochemical production of mononuclear metal carbonyl radicals is well known.\textsuperscript{10,92} Appropriate trapping agents have been employed in many dinuclear metal carbonyl photolyses to provide evidence for the formation of mononuclear metal carbonyl fragments. In the photolysis of [CpFe(CO)(\(\mu\)-CO)]\textsubscript{2} and CCl\textsubscript{4}, CpFe(CO)\textsubscript{2}Cl is formed which implies the existence of the 17 electron radical intermediate, CpFe(CO)\textsubscript{2}*\textsuperscript{110}. However, the photolysis of [CpFe(CO)]\textsubscript{2}(\(\mu\)-CO)(\(\mu\)-CHCH\textsubscript{3}) with CCl\textsubscript{4} also forms CpFe(CO)\textsubscript{2}Cl with no apparent formation of other cyclopentadienyl or carbonyl-containing species.\textsuperscript{22} It has been established that [CpFe(CO)]\textsubscript{2}(\(\mu\)-CO)(\(\mu\)-CHCH\textsubscript{3}) does not undergo homolytic cleavage, and additional kinetic studies which provide evidence that CCl\textsubscript{4} reacts with [CpFe]\textsubscript{2}(\(\mu\)-CO)\textsubscript{2}(\(\mu\)-CHCH\textsubscript{3}). In addition, Caspar and Meyer have demonstrated that [CpFe]\textsubscript{2}(\(\mu\)-CO)\textsubscript{3} reacts with CCl\textsubscript{4} to form CpFe(CO)\textsubscript{2}Cl.\textsuperscript{14} Thus, it is apparent that Cl\textsuperscript{*} abstraction from CCl\textsubscript{4} in dinuclear carbonyl systems does not necessarily result from the reaction of
CCl4 with photochemically produced radicals.\textsuperscript{22} The CO-loss species of Mn\textsubscript{2}(CO)\textsubscript{10}, Mn\textsubscript{2}(CO)\textsubscript{9}, has also been shown to react with CCl\textsubscript{4}.\textsuperscript{111} With such a caution, CCl\textsubscript{4} is still a suitable initial trapping agent to begin probing the possibility of photochemical radical formation in solution.

1. CCl\textsubscript{4} and [CpCo(CO)]\textsubscript{2}(\mu-CH\textsubscript{2})

When [CpCo(CO)]\textsubscript{2}(\mu-CH\textsubscript{2}) and CCl\textsubscript{4} in CD\textsubscript{3}CN solution are irradiated at 0°C, the NMR peaks due to [CpCo(CO)]\textsubscript{2}(\mu-CH\textsubscript{2}) (6.67 and 4.96) decrease while new peaks emerge (Figure 3.78). In particular, a peak at 5.15 ppm grows in, which corresponds to CpCo(CO)\textsubscript{2} in CD\textsubscript{3}CN. In addition, a broad peak grows and shifts while narrowing to 5.49 ppm. This peak apparently corresponds to CH\textsubscript{2}Cl\textsubscript{2} in CD\textsubscript{3}CN, which has been confirmed by a genuine sample. This reaction indicates that [CpCo(CO)]\textsubscript{2}(\mu-CH\textsubscript{2}) is cleaved into mononuclear metal fragments and methylene-based products.

A possible first step in this mechanism may be chlorine abstraction by the diradical of [CpCo(CO)]\textsubscript{2}(\mu-CH\textsubscript{2}) to form Cl(CO)Co(\mu-CH\textsubscript{2})Co(CO)Cl. In support of this idea, Brown and coworkers studied the photolysis of [Re(CO)\textsubscript{4}]\textsubscript{2}(\mu-PPh\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2}) in the presence of CCl\textsubscript{4}. They found that this reaction yields Cl(CO)\textsubscript{4}RePPh\textsubscript{2}CH\textsubscript{2}Ph\textsubscript{2}PRe(CO)\textsubscript{4}Cl,
Figure 3.78: $^1$H NMR spectra of a $[\text{CpCo(CO)}]_2(\mu-\text{CH}_2)$ and $1\%\text{CCl}_4$ reaction mixture at various increments of irradiation in $\text{CDCN}_3$ at $0^\circ\text{C}$. 
indicating halogen abstraction by a diradical intermediate, 
•Re(CO)_4PPh_2CH_2Ph_2P(CO)_4Re•.\textsuperscript{112}

Subsequent photolysis of the Co-CH_2 bond in the double-abstraction product and an additional chlorine abstraction could yield CH_2Cl_2 and CpCo(CO)Cl_2. The latter complex is an unstable mononuclear complex\textsuperscript{113} that might decompose to form CpCo(CO)_2 under photolytic conditions. This proposed mechanism is shown in Figure 3.79.

The green solid that is produced in these reactions is additional support for the formation of CpCo(CO)Cl_2. This solid precipitated out of solution in non-polar solvents, such as benzene. The formation of CpCo(CO)Cl_2 has previously been reported,\textsuperscript{113} however, the species was not characterized because it decomposed above -20\textdegree C to form a green amorphous solid. However, CpCo(CO)Br_2 and CpCo(CO)I_2 are characterized.\textsuperscript{113} Because CpCo(CO)I_2 is a stable, solid at room temperature, reactions of [CpCo(CO)]_2(\mu-CH_2) with iodocarbons were performed to see if CpCo(CO)I_2 would be one of the photochemical products.

Upon adding Cl_4 or I_2 to [CpCo(CO)]_2(\mu-CH_2) in THF solution an immediate thermal reaction was noted. The initial red solution
Figure 3.79: Proposed scheme of photochemical and thermal reaction pathways of [CpCo(CO)]$_2$(μ-CH$_2$) and CCl$_4$. 

CH$_2$Cl$_2$ + CpCo(CO)Cl$_2$ → CpCo(CO)$_2$ and "decomposition products"
immediately appeared green in color. The formation of CpCo(CO)I₂ was confirmed by an IR band at 2069 cm⁻¹ in THF, which correlates to the IR of CpCo(CO)I₂ prepared by the literature methods.⁴⁹ The significant NMR band of the solution residue was either 4.27 or 4.31 ppm in C₆D₆ or 5.68 ppm in CDCl₃. The former value compares well to the value determined from CpCo(CO)I₂ prepared by the literature method, 4.33 ppm, while the latter compares well to the literature value, 5.65 ppm.⁴⁹ There is an additional IR peak at 1875 cm⁻¹ which disappears by 30 minutes, suggesting an intermediate may be involved in the reaction.

The reaction of [CpCo(CO)]₂(μ-CH₂) with CH₂I₂ is not as straightforward as the reaction of [CpCo(CO)]₂(μ-CH₂) with Cl₄ and I₂. Certain experiments show no thermal reactivity via IR except a slight decrease in the amount of [CpCo(CO)]₂(μ-CH₂) after long reaction times. However, several other experiments showed greater reactivity. For example, after 30 minutes in THF solution, a new peak at 2021 cm⁻¹ was noted with a concomitant slight decrease in the [CpCo(CO)]₂(μ-CH₂) peak at 1953 cm⁻¹. In addition, an NMR experiment showed the formation of a
small peak at 5.13 ppm in d$_8$-THF within 20 minutes of the reaction. This peak corresponds to CpCo(CO)$_2$.

The amount of thermal reactivity of [CpCo(CO)$_2$(μ-CH$_2$)] and CH$_2$I$_2$ is insignificant compared to the photochemical reactivity. After only 10 minutes of photolysis in toluene solution, distinct formation of CpCo(CO)I$_2$ is observed via IR spectroscopy (2065 cm$^{-1}$). This band shifts to 2069 cm$^{-1}$ after 30 minutes of irradiation. A THF solution in a closed quartz cuvette showed formation of both CpCo(CO)$_2$ and CpCo(CO)I$_2$, as shown by IR bands at 2022 and 1957 cm$^{-1}$ and 2069 cm$^{-1}$, respectively. In a simultaneous reaction, a Pyrex flask open to an Ar bubbler shows only a slight change, with a peak appearing at 2022 cm$^{-1}$. The Pyrex system was then closed and the solution was irradiated for 135 minutes. The experiment resulted in a green solution that contains CpCo(CO)$_2$ and CpCo(CO)I$_2$, as suggested by IR bands at 2022, 1957, and 2069 cm$^{-1}$.

During this same 135 minute period, the green solution in the quartz cuvette underwent dark thermal reactions. The solution changed to a purple color and showed the IR band for CpCo(CO)I$_2$ at 2069 cm$^{-1}$ as the only significant product. Thus, CpCo(CO)$_2$ does readily react thermally
with the photochemical product of CH$_2$I$_2$, I$_2$. The reaction of I$_2$ with
CpCo(CO)$_2$ is the literature method of preparation of CpCo(CO)I$_2$.\textsuperscript{49}

The thermal reaction noted of [CpCo(CO)]$_2$(μ-CH$_2$) with Cl$_4$ and I$_2$
excludes the possibility of studying its photochemical reactivity with
[CpCo(CO)]$_2$(μ-CH$_2$). The slight thermal reactivity of CH$_2$I$_2$ with
[CpCo(CO)]$_2$(μ-CH$_2$) is slow enough that their photochemical reactivity
could be studied. However, the photochemical reaction between CH$_2$I$_2$ and
[CpCo(CO)]$_2$(μ-CH$_2$) may be due to the generation of I$_2$ upon photolysis of
CH$_2$I$_2$. If I$_2$ were produced, it could initiate a facile thermal reaction
between I$_2$ and [CpCo(CO)]$_2$(μ-CH$_2$). Both CpCo(CO)$_2$ and CpCo(CO)I$_2$ are
for all intents and purposes present immediately upon irradiation of CH$_2$I$_2$
and [CpCo(CO)]$_2$(μ-CH$_2$). Because irradiation of [CpCo(CO)]$_2$(μ-CH$_2$)
alone does not produce CpCo(CO)$_2$, the presence of CH$_2$I$_2$ during
irradiation or its photoproduct must interact with [CpCo(CO)]$_2$(μ-CH$_2$) to
initiate a reaction. Whether [CpCo(CO)]$_2$(μ-CH$_2$) directly abstracts I from
CH$_2$I$_2$ or I$_2$ has not been determined at this time.

The reactions of [CpCo(CO)]$_2$(μ-CH$_2$) with the iodocarbon complexes,
CCl$_4$ and CH$_2$I$_2$, do not explicitly show radical formation while Cl$_4$ and I$_2$
demonstrate facile thermal reactions. The formation of \( \text{CpCo(CO)}_2 \) and \( \text{CH}_2\text{Cl}_2 \) from the irradiation of \( [\text{CpCo(CO)}]_2(\mu-\text{CH}_2) \) and \( \text{CCl}_4 \) does suggest a possible radical mechanism, perhaps even a diradical. However, it is clearly known that halogen abstraction does not necessitate organometallic radical formation.\(^{10a}\) It is clear that this reaction is not definitive and other probes should be pursued, such as faster transient spectroscopic methods.

D. Crossover Reactions

Photochemical crossover reactions are another test for the formation of mononuclear radical species. When \( [\text{CpFe(CO)}(\mu-\text{CO})]_2 \) and \( [\text{Cp}^*\text{Fe(CO)}(\mu-\text{CO})]_2 \) are irradiated, a mixture of \( [\text{CpFe(CO)}(\mu-\text{CO})]_2 \), \( [\text{Cp}^*\text{Fe(CO)}(\mu-\text{CO})]_2 \), and \( [\text{Cp}^*(\text{CO})\text{Fe(\mu-CO)}_2\text{Fe(CO)Cp}] \) is produced in a 1:1:2 ratio. This ratio is the one expected if the reaction occurs through mononuclear radical formation and subsequent recombination. Thus, the photochemical formation of mixed crossover dinuclear species has been interpreted as an indication of the formation of mononuclear species.\(^{114}\)

1. \( [\text{CpCo(CO)}]_2(\mu-\text{CH}_2) \) with \( [\text{CpFe(CO)}(\mu-\text{CO})]_2 \)

A preliminary room temperature irradiation of \( [\text{CpCo(CO)}]_2(\mu-\text{CH}_2) \) and \( [\text{CpFe(CO)}(\mu-\text{CO})]_2 \) in \( \text{C}_6\text{D}_6 \) resulted in the formation of several new
peaks at 4.52 and 4.41 ppm. The IR spectrum of the reaction residue in hexane solvent showed a new weak CO band at 1830 cm\(^{-1}\) (Figure 3.80). The reported CO stretch of the CO loss product of \([\text{CpFe}(\text{CO})(\mu-\text{CO})]_2\), \([\text{CpFe}]_2(\mu-\text{CO})_3\), is 1823 cm\(^{-1}\) in cyclohexane at 295 K.\(^{15b}\) However, this product cannot be the one present because it has only a 3 s half-life at room temperature.\(^{14,15b,16}\) The CO band of the new product corresponds to a bridging CO while the new NMR resonances are indicative of Cp protons, 4.41 and 4.52 ppm in C\(_6\)D\(_6\) (Figure 3.81). These proton resonances are found between those of the Cp peaks of the respective parent peaks, \([\text{CpFe}(\text{CO})(\mu-\text{CO})]_2\) at 4.23 ppm and \([\text{CpCo}(\text{CO})]_2(\mu-\text{CH}_2)\) at 4.64 ppm. Where \([\text{CpFe}(\text{CO})(\mu-\text{CO})]_2\) and \([\text{Cp'Fe}(\text{CO})(\mu-\text{CO})]_2\) are irradiated, two out of three of the crossover compound proton peaks occur between those of the respective parent complexes.\(^{115}\)

The emergence of these new peaks indicates the possibility of the formation of a mixed metal compound with at least one bridging CO group between the two metal atoms. The monomer \(\text{CpCo}(\text{CO})_2\) has a single proton NMR resonance at 4.42 ppm in C\(_6\)D\(_6\); however, the reaction between \([\text{CpCo}(\text{CO})]_2(\mu-\text{CH}_2)\) and \([\text{CpFe}(\text{CO})(\mu-\text{CO})]_2\) appears relatively in which no decomposition compounds of the "\(\text{CpCo}(\text{CO})(\text{CH}_2)\)" fragment are
Figure 3.80: Infrared spectrum of the photochemical reaction residue of
\([CpCo(CO)]_2(\mu-CH_2)\) and \([CpFe(CO)(\mu-CO)]_2\) in hexane.
Figure 3.81: $^1$H NMR spectrum of the reaction mixture of [CpCo(CO)]$_2$(μ-CH$_2$) and [CpFe(CO)(μ-CO)]$_2$ in C$_6$D$_6$ after 40 minutes of irradiation.
apparent. There is no evidence of the existence of a new methylene-bridged complex in the $^1$H NMR.

CpFe(µ-CO)$_3$CoCp is a possible structure of the new product, which would have a bridging CO resonance on the order of that of [CpFe]$_2$(µ-CO)$_3$ and two inequivalent Cp rings. However, CpFe(µ-CO)$_3$CoCp, like [CpFe]$_2$(µ-CO)$_3$, would likely be paramagnetic due to a triplet ground state. Thus, the obtained $^1$H NMR would have broadened peaks, which were not observed in the $^1$H NMR of the reaction mixture. In addition, CpFe(µ-CO)$_3$CoCp could result from the combination of CpFe(CO)$_2$ and CpCo(CO), two 17 electron radicals. However, the resulting complex, CpFe(µ-CO)$_3$CoCp, would not follow the 18 electron rule which suggests the structure is unlikely. The peak at 4.41 ppm could be CpCo(CO)$_2$. The CpCo(CO)$_2$ complex would have been pulled off via vacuum before the IR spectrum was obtained explaining the absence of its peaks in the IR spectrum. However, if CpCo(CO)$_2$ were the product, the assignment of the other Cp peak is problematic without any indication of the fate of the methylene protons.

In light of the transient absorption work, reactivity of this type would be unexpected. If mononuclear radical fragments were formed
additional decomposition products would be expected. Scale up of this reaction and subsequent column separation may prove interesting with regard to the possible photochemical radical formation of \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\).

In general, the solution reactivity studies are preliminary and inconclusive. They do, however, point to some interesting possibilities with regard to possible radical reactivity whereas the transient absorption spectroscopy does not indicate any radical activity.

D. Conclusion
As expected, \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\), \([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\), and \([\text{Cp}^*\text{Fe(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) exhibit a rich photochemistry like other dinuclear organometallic complexes. They clearly exhibited the formation of multiple CO-loss complexes within low temperature hydrocarbon matrices. With the exception of \([\text{CpFe(CO)}(\mu-\text{CO})]_2\), these complexes are the only other cyclopentadienyl carbonyl dinuclear species that have been reported to undergo sequential photochemical CO-loss. Although some compounds, eg. \([\text{CpMo(CO)}]_2\), undergo double-CO loss, the second CO group lost is presently attributed to a thermal rather than photochemical process.
All three complexes form a single-CO-loss species: $[\text{CpCo}]_2(\mu-CO)(\mu-\text{CH}_2)$, $[\text{CpMn}(\text{CO})]_2(\mu-\text{CO})(\mu-\text{CH}_2)$, and $[\text{Cp}^*\text{Fe}]_2(\mu-\text{CO})(\mu-\text{CH}_2)$, respectively. Like $[\text{Cp}^*\text{Fe}(\text{CO})]_2(\mu-\text{CO})(\mu-\text{CH}_2)$, $[\text{CpCo}(\text{CO})]_2(\mu-\text{CH}_2)$ and $[\text{CpMn}(\text{CO})]_2(\mu-\text{CH}_2)$ undergo double CO-loss forming $[\text{CpCo}]_2(\mu-\text{CH}_2)$ and $[\text{CpMn}(\text{CO})]_2(\mu-\text{CH}_2)$. In addition, $[\text{CpMn}(\text{CO})]_2(\mu-\text{CH}_2)$ appears to undergo an additional CO-loss to form a triple-CO-loss product, $[\text{CpMn}]_2(\mu-\text{CO})(\mu-\text{CH}_2)$. This species is isostructural with the proposed double-CO-loss product of $[\text{Cp}^*\text{Fe}(\text{CO})]_2(\mu-\text{CO})(\mu-\text{CH}_2)$, $[\text{Cp}^*\text{Fe}]_2(\mu-\text{CO})(\mu-\text{CH}_2)$.

The apparent thermal reactivity of $[\text{Cp}^*\text{Fe}]_2(\mu-\text{CO})(\mu-\text{CH}_2)$ with $\text{P}(n-\text{Bu})_3$ at 96 K in the matrix is particularly exciting because it appears to form a bisphosphine substituted product, $[\text{Cp}^*\text{Fe}[\text{P}(n-\text{Bu})_3]]_2(\mu-\text{CO})(\mu-\text{CH}_2)$. While the photochemical formation of bisphosphite substituted dinuclear carbonyl complexes are known such as $[\text{CpFe}[\text{P(OMe)}_3]]_2(\mu-\text{CO})_2$, no analogous bisphosphine complexes are known. The reason for this is not clear, but apparently a method of synthesis has been found through low temperature matrix photolyses. The predominant formation of the bisphosphine complex suggests that the assertion of the formation of a double-CO-loss product is reasonable in a low temperature matrix.
Further, the presence of this complex, \([\text{Cp}^*\text{Fe}\{\text{P}(\text{n-Bu})_3\}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\), upon warming to room temperature may provide the opportunity for additional spectroscopic analysis and understanding of why this type of complex as to now have been unknown.

The formation of the DMAD insertion product of \([\text{CpCo}(\text{CO})]_2(\mu-\text{CH}_2)\), \(\text{Cp}_2\text{Co}_2(\mu-\text{CH}_2)(\mu-\text{C}(\text{O})\text{C}_2\text{R}_2)\) \((\text{R} = \text{CO}_2\text{Me})\), also provides evidence of the formation of a CO-loss species. The mechanism proposed for the formation of these species involves a CO-loss intermediate. While there is evidence for insertion between the hydrocarbyl carbon and cobalt atom, the proposed structure of the insertion product that was isolated involves the insertion of the alkyne, DMAD, between a carbonyl carbon and cobalt atom. This observation is exciting because this type of insertion has never been reported before in an alkylidene-bridged complex. The DMAD insertion product of \([\text{CpFe}(\text{CO})]_2(\mu-\text{CO})(\mu-\text{CHCH}_3)\), \(\text{Cp}_2\text{Fe}_2(\text{CO})(\mu-\text{CO})(\mu-\eta^1-\eta^3\text{C}(\text{R})\text{C}(\text{R})\text{CHCH}_3)\) \((\text{R} = \text{CO}_2\text{Me})\), inserts exclusively between the hydrocarbyl carbon and iron atoms;\(^{26}\) no evidence for a product involving insertion between a carbonyl carbon and iron atom were found.

These results suggest that dinuclear cyclopentadienyl carbonyl metal species may indeed be “tuned” to produce specific reactivities. Whereas the CO-loss species of \([\text{CpCo}(\text{CO})]_2(\mu-\text{CH}_2)\), \([\text{CpCo}]_2(\mu-\text{CO})(\mu-\eta^1-\eta^3\text{C}(\text{R})\text{C}(\text{R})\text{CHCH}_3)\)
contains only two bridging ligands, the CO-loss species of

\[ [\text{CpFe(CO)}]_2(\mu-\text{CO})(\mu-\text{CHCH}_3), \quad [\text{CpFe}]_2(\mu-\text{CO})_2(\mu-\text{CHCH}_3) \]

contains three bridging groups as well as a different metal and a slightly bulkier hydrocarbyl-bridge substituent. Any one or combination of these differences may invoke a different attack on the dinuclear framework. In the case of \[ [\text{CpFe}]_2(\mu-\text{CO})_2(\mu-\text{CHCH}_3) \], this combination appears to inhibit insertion into the hydrocarbyl carbon-iron bond. The proposed intermediate in these substitution reactions shown in Figure 3.65 involving the \( \eta^2 \) bound alkyne may be involved. The \[ [\text{CpCo}]_2(\text{CO})(\eta^2-\text{DMAD})(\mu-\text{CH}_2) \] intermediate contains no bridging carbonyls while the intermediate \[ [\text{CpFe}]_2(\text{CO})(\eta^2-\text{DMAD})(\mu-\text{CO})(\mu-\text{CHCH}_3) \] intermediate still contains a bridging carbonyl ligand. This structural difference, which has electronic implications as well, may elicit preferential insertion into the hydrocarbyl carbon and metal atoms. The electron charge on the methylene carbon may be altered or the increased mobility of the CO ligand may also have an effect on the dominate or exclusive resultant product(s).

Transient absorption spectroscopy also shows strong evidence for the formation of CO-loss species of \[ [\text{Cp*Fe(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2) \] and \[ [\text{CpCo(CO)}]_2(\mu-\text{CH}_2) \]. The transient absorptions can be observed for those
wavelengths at which they absorb more strongly than their parent complexes. The transient absorption spectra also indicate that like other dinuclear alkylidene-bridged transition-metal complexes such as [CpFe(CO)]$_2$(μ-CO)(μ-CHCH$_3$)$_2$ photolysis results only in the formation of a CO-loss product; mononuclear radicals are not formed. There are no short-lived ($t_{1/2}$ ca. 25 μs)$^{14,15a,16}$ species observed in the transient spectra. In addition, when the absorption is followed at the wavelength maximum associated with the CO-loss species, both [Cp*Fe(CO)]$_2$(μ-CO)(μ-CH$_2$)$_2$ and [CpCo(CO)]$_2$(μ-CH$_2$)$_2$ show the characteristic abrupt rise in absorption associated with the formation of [Cp*Fe]$_2$(μ-CO)$_2$(μ-CH$_2$)$_2$ and [CpCo]$_2$(μ-CO)(μ-CH$_2$)$_2$, respectively. This rise is followed by a slow decrease in absorption as CO-loss products react with CO in solution to reform their parent complexes, which absorb less strongly at these wavelengths.

The absorption trace obtained for [CpFe(CO)(μ-CO)]$_2$ under the same conditions demonstrates a very different shape. In this case, the same abrupt rise is noted upon initial formation of [CpFe]$_2$(μ-CO)$_3$. The rise seems to be less instantaneous than in the cases of [Cp*Fe(CO)]$_2$(μ-CO)(μ-CH$_2$)$_2$ and [CpCo(CO)]$_2$(μ-CH$_2$)$_2$, however, and a steady increase is noted in the absorption rather than a decrease. This behavior can be
explained in terms of the known photochemical products of 
[CpFe(CO)(μ-CO)]₂, a long lived CO-loss species, [CpFe]₂(μ-CO)₃, and a 
short lived radical species, CpFe(CO)₂⁺. Thus, the initial absorption rise 
is less abrupt because CpFe(CO)₂⁺ is also formed, which absorbs less 
strongly than either [CpFe(CO)(μ-CO)]₂ or [CpFe]₂(μ-CO)₃. As this short 
lived radical recombines to form [CpFe(CO)(μ-CO)]₂, the absorption 
increases. The increase of absorption due to this process is stronger than 
the decrease in absorption due to the reaction of [CpFe]₂(μ-CO)₃ and CO to 
form [CpFe(CO)(μ-CO)]₂. Thus, the almost vertical nature and subsequent 
decrease in absorptions of the absorption traces of [Cp*Fe(CO)]₂(μ-CO)(μ- 
CH₂) and [CpCo(CO)]₂(μ-CH₂) provide further evidence against the 
formation of radicals in these species and additional support for the 
formation of CO-loss species.

It is apparent that these methylene-bridged species exhibit the 
same photochemical processes as [CpFe(CO)]₂(μ-CO)(μ-CHCH₃) in that no 
evidence of a radical process is observed while facile CO-loss is observed. 
These species are efficient at CO-loss such that sequential CO-loss in a low 
temperature matrix is possible. This has lead to the first bisphosphine 
substituted complex reported. Further, the dinuclear framework has been
tuned to enable alternative CO-loss in alkyne insertion, in that DMAD has been observed to insert between a carbonyl carbon and metal atom rather than the previously reported exclusive insertion into the hydrocarbyl carbon and metal bond of another alkylidene-bridged dinuclear transition-metal complex, \([\text{CpFe(CO)}]_2(\mu-\text{CO})(\mu-\text{CHCH}_3)\)\(^{26}\) which may be due to the nature of the binding of the CO groups in the proposed intermediate. Thus, these systems are ideal to study in that the general reaction types they undergo can be controlled while allowing slight modifications to allow slightly different reactivity within the defined reaction types.

E. Future Directions

Probably the most exciting future direction to take with regard to this research is in the matrix photochemistry reactivity of \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\), \([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\), and \([\text{Cp*Fe(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\). The initial study of the reactivity of the double-CO-loss species of \([\text{Cp*Fe(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\), \([\text{Cp*Fe}]_2(\mu-\text{CO})_2(\mu-\text{CH}_2)\), with \(\text{P(n-Bu)}_3\) which resulted in the bisphosphine complex, \([\text{Cp*Fe[P(n-Bu)}_3]_2(\mu-\text{CO})(\mu-\text{CH}_2)\). This complex may form directly from \([\text{Cp*Fe}]_2(\mu-\text{CO})_2(\mu-\text{CH}_2)\) rather than the
monosubstituted complex; thus, extending these reactivity studies to bidentate phosphine ligands may provide insight into this mechanistic question. In addition, the CO-loss complexes of both \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) and \([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\) would be expected to undergo facile reaction with phosphines. The possibility exists that \([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\) may add more than two phosphines.

The photochemical reaction of DMAD with both \([\text{Cp}^*\text{Fe(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) and \([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\) would be interesting. Both \([\text{Cp}^*\text{Fe(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) and \([\text{CpFe(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) may form exclusively hydrocarbyl carbon-metal atom insertion products like both \([\text{Cp}^*\text{Fe(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_3)\). However, type(s) of insertion product that \([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\) would form could be revealing. The insertion intermediate would contain only a hydrocarbyl bridge; thus, preferential insertion into the carbonyl \(C\) and metal atom may occur analogously to the \([\text{CpCo(CO)}]_2(\mu-\text{CH}_2)\) reaction. If such insertion occurred, it would add support to the suggestion that the nature of the bonding mode of the CO does influence the resultant product(s). Studying the photochemical reactions of \([\text{CpMn(CO)}]_2(\mu-\text{CH}_2)\) and \([\text{Cp}^*\text{Fe(CO)}]_2(\mu-\text{CO})(\mu-\text{CH}_2)\) with DMAD would allow for the observation of trends based on bonding modes.
and, therefore, could have interesting implications in terms of the factors that influence the type of insertion that occurs in these complexes.
Appendix A

NMR Data Saving Instruction Sheet
**NMR File Saving**

**Temporary Storage:** Type WR `<filename>`

**Transferring Files to 1.44Mb Diskette:**

Channels:  
0 for transfer from AM-250-11  
2 for transfer from AC-300  
4 for transfer from AM-250-1

**On the 250-1:**

1. Type **CTRL-X** (the LCD will change from a “1U:” prompt to “2S:”)
2. Type **LIGHTNET** then press **RET**
3. Type 4 then press **RET** (4 in the channel number for the 250-1)

**Go to the Data Station:**

4. Type **CTRL-X** (the LCD will change from a “1U:” prompt to “2S:”)
5. Type **LIGHTNET** then press **RET**
6. Type 4 then press **RET**

**Go Back to the 250-1:**

8. Type **S4<filename>** (no space; the terminal will add it automatically)  
   then press **RET**  
   [Type S2 for the AC-300 or S0 for the AM-250-11]

Continue until all files are transferred

9. Type **CTRL-E**
10. Type **CTRL-X** (the LCD will change from a “1S;” prompt to “1U;”)

Go to the Data Station:

11. Type **CTRL-E**
12. Type **CTRL-X**  (the LCD will change from a “1S:” prompt to “1U:”)
13. Type **CTRL-X**  (the LCD will change from a “1U:” prompt to “2S:”)
14. Type **NMRNET** then press **RET**

Go to the PC:

15. Double Click on the NMRNET icon (prompt is “PC2NMR:”)
16. Type **cd a:**
17. Put formatted disk into drive a
18. Type **GET <filename>** (the file(s) will be saved on the disk in drive A)
   (To transfer files EMM6.16A through I, type EMM6.16?)
19. Type **cd c:**
20. You can now close out of the PC program. Turn off the screen.

Go back to the data station:

21. Type **CTRL-E**
22. Type **CTRL-X**
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